

## TENT COOPERATION TRE. Y

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
United States Patent and Trademark  
Office  
Box PCT  
Washington, D.C.20231  
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year)  
11 May 2000 (11.05.00)

International application No.  
PCT/US99/15181

Applicant's or agent's file reference  
901713ETT

International filing date (day/month/year)  
06 July 1999 (06.07.99)

Priority date (day/month/year)  
06 July 1998 (06.07.98)

## Applicant

AYERS, William, M.

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:  
01 February 2000 (01.02.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

R. Forax

Telephone No.: (41-22) 338.83.38

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## PATENT COOPERATION TREATY

09/720663

PCT

NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

GANDY, Kenneth, A.  
Woodard, Emhardt, Naughton,  
Moriarty & McNett  
Bank One Center/Tower  
Suite 3700  
111 Monument Circle  
Indianapolis, IN 46204  
ETATS-UNIS D'AMERIQUE

Date of mailing (day/month/year) 12 January 2001 (12.01.01)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference 901713ETT	
International application No. PCT/US99/15181	International filing date (day/month/year) 06 July 1999 (06.07.99)

## 1. The following indications appeared on record concerning:

☒ the applicant ☒ the inventor ☐ the agent ☐ the common representative

## Name and Address

AYERS, William, M.  
372 Carter Road  
Princeton, NJ 08540  
United States of America

## State of Nationality

US

## State of Residence

US

Telephone No.

Facsimile No.

Teleprinter No.

## 2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person ☐ the name ☒ the address ☐ the nationality ☐ the residence

## Name and Address

AYERS, William, M.  
30 Charlton Street  
New York  
NY 10014  
United States of America

## State of Nationality

US

## State of Residence

US

Telephone No.

Facsimile No.

Teleprinter No.

## 3. Further observations, if necessary:

## 4. A copy of this notification has been sent to:

☒ the receiving Office ☐ the designated Offices concerned  
☐ the International Searching Authority ☒ the elected Offices concerned  
☒ the International Preliminary Examining Authority ☐ other:

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Sean Taylor

Telephone No.: (41-22) 338.83.38

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RECEIVED

ENT COOPERATION TRE

SEP 22 1999

Woodard, Emhardt, Naughton,  
Moriarty & McNett

PCT

From the INTERNATIONAL BUREAU

NOTIFICATION CONCERNING  
SUBMISSION OR TRANSMITTAL  
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

To:

GANDY, Kenneth, A.  
Woodard, Emhardt, Naughton,  
Moriarty & McNett  
Bank One Center/Tower  
Suite 3700  
111 Monument Circle  
Indianapolis, IN 46204  
ÉTATS-UNIS D'AMÉRIQUE

Date of mailing (day/month/year) 02 September 1999 (02.09.99)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference 901713ETT	
International application No. PCT/US99/15181	International filing date (day/month/year) 06 July 1999 (06.07.99)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 06 July 1998 (06.07.98)
Applicant ELECTRON TRANSFER TECHNOLOGIES, INC. et al	

- The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
- This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
- An asterisk(\*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
- The letters "NR" appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
06 July 1998 (06.07.98)	60/091,737	US	31 Augu 1999 (31.08.99)

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer

Juan Cruz

Telephone No. (41-22) 338.83.38

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## TENT COOPERATION TREATY

JAN 25 2000

PCT

NOTICE INFORMING THE APPLICANT OF THE  
COMMUNICATION OF THE INTERNATIONAL  
APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

To:

GANDY, Kenneth, A.  
Woodard, Emhardt, Naughton,  
Moriarty & McNett  
Bank One Center/Tower  
Suite 3700  
111 Monument Circle  
Indianapolis, IN 46204  
ÉTATS-UNIS D'AMÉRIQUE

Date of mailing (day/month/year) 13 January 2000 (13.01.00)		IMPORTANT NOTICE	
Applicant's or agent's file reference 901713ETT			
International application No. PCT/US99/15181	International filing date (day/month/year) 06 July 1999 (06.07.99)	Priority date (day/month/year) 06 July 1998 (06.07.98)	
Applicant ELECTRON TRANSFER TECHNOLOGIES, INC. et al			

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:  
CN,JP,US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:  
None

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on 13 January 2000 (13.01.00) under No. WO 00/01615

**REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)**

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

**REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))**

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 740.14.35	Authorized officer J. Zahra Telephone No. (41-22) 338.83.38
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From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

MAY 01 2000

PCT

Woodard, Emhardt, Naughton,  
Moriarty & McNett

To:

KENNETH A. GANDY  
WOODARD, EMHARDT, NAUGHTON, MORIARTY &  
MCNETT; BANK ONE CENTER/TOWER  
111 MONUMENT CIRCLE, SUITE 3700  
INDIANAPOLIS IN 46204

NOTIFICATION OF RECEIPT  
OF DEMAND BY COMPETENT INTERNATIONAL  
PRELIMINARY EXAMINING AUTHORITY

(PCT Rule 593(e) and 61.1(b), first sentence  
and Administrative Instructions, Section 601(a))

Date of mailing  
(day/month/year)

27 APR 2000

Applicant's or agent's file reference  
901713ETT

## IMPORTANT NOTIFICATION

International application No.  
PCT/US99/15181

International filing date (day/month/year)  
06 JUL 99

Priority date (day/month/year)  
06 JUL 98

Applicant

ELECTRON TRANSFER TECHNOLOGIES, INC.

1. The applicant is hereby **notified** that this International Preliminary Examining Authority considers the following date as the date of receipt of the demand for international preliminary examination of the international application:

01 FEB 2000

2. That date of receipt is:



the actual date of receipt of the demand by this Authority (Rule 61.1(b)).



the actual date of receipt of the demand on behalf of this Authority (Rule 59.3(e)).



the date on which this Authority has, in response to the invitation to correct defects in the demand (Form PCT/IPEA/404), received the required corrections.

3. ☐ **ATTENTION:** That date of receipt is **AFTER** the expiration of 19 months from the priority date. Consequently, the election(s) made in the demand does (do) not have the effect of postponing the entry into the national phase until 30 months from the priority date (or later in some Offices) (Article 39(1)). Therefore, the acts for entry into the national phase must be performed within 20 months from the priority date (or later in some Offices) (Article 22). For details, see the *PCT Applicant's Guide*, Volume II.



(If applicable) This notification confirms the information given by telephone, facsimile transmission or in person on:

4. Only where paragraph 3 applies, a copy of this notification has been sent to the International Bureau.

Name and mailing address of the IPEA/US  
Assistant Commissioner for Patents  
Box PCT  
Washington, D.C. 20231  
Facsimile No.

Attn: IPEA/US

Authorized officer

Telephone No.

703-305-3743

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## PCT COOPERATION TREATY

PCT

INFORMATION CONCERNING ELECTED  
OFFICES NOTIFIED OF THEIR ELECTION

(PCT Rule 61.3)

From the INTERNATIONAL BUREAU

To:

GANDY, Kenneth, A.  
Woodard, Emhardt, Naughton,  
Moriarty & McNett  
Bank One Center/Tower  
Suite 3700  
111 Monument Circle  
Indianapolis, IN 46204  
ETATS-UNIS D'AMERIQUE

RECEIVED

MAY 30 2000

Woodard, Emhardt, Naughton,  
Moriarty & McNett

Date of mailing (day/month/year) 11 May 2000 (11.05.00)		IMPORTANT INFORMATION	
Applicant's or agent's file reference 901713ETT			
International application No. PCT/US99/15181	International filing date (day/month/year) 06 July 1999 (06.07.99)	Priority date (day/month/year) 06 July 1998 (06.07.98)	
Applicant ELECTRON TRANSFER TECHNOLOGIES, INC. et al			

1. The applicant is hereby informed that the International Bureau has, according to Article 31(7), notified each of the following Offices of its election:

National :CN,JP,US

2. The following Offices have waived the requirement for the notification of their election; the notification will be sent to them by the International Bureau only upon their request:

None

3. The applicant is reminded that he must enter the "national phase" before the expiration of 30 months from the priority date before each of the Offices listed above. This must be done by paying the national fee(s) and furnishing, if prescribed, a translation of the international application (Article 39(1)(a)), as well as, where applicable, by furnishing a translation of any annexes of the international preliminary examination report (Article 36(3)(b) and Rule 74.1).

Some offices have fixed time limits expiring later than the above-mentioned time limit. For detailed information about the applicable time limits and the acts to be performed upon entry into the national phase before a particular Office, see Volume II of the PCT Applicant's Guide.

<p>The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland</p> <p>Facsimile No. (41-22) 740.14.35</p>	<p>Authorized officer: R. Forax</p> <p>Telephone No. (41-22) 338.83.38</p>
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**PCT****REQUEST**

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference  
(if desired) (12 characters maximum)

901713ETT

**Box No. I TITLE OF INVENTION**

METHOD AND APPARATUS FOR THE PREPARATION OF HIGH PURITY PHOSPHINE OR OTHER GAS

**Box No. II APPLICANT**

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

ELECTRON TRANSFER TECHNOLOGIES, INC.  
155 Campus Drive  
P.O. Box 5812  
Edison, New Jersey 08818-5812 US

☐ This person is also inventor.

Telephone No.

Facsimile No.

Teleprinter No.

State (that is, country) of nationality:  
USState (that is, country) of residence:  
USThis person is applicant  
for the purposes of:☐ all designated  
States☒ all designated States except  
the United States of America☐ the United States  
of America only☐ the States indicated in  
the Supplemental Box**Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)**

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

AYERS, William M.  
372 Carter Road  
Princeton, New Jersey 08540 US

This person is:

☐ applicant only☒ applicant and inventor☐ inventor only (If this check-box  
is marked, do not fill in below.)State (that is, country) of nationality:  
USState (that is, country) of residence:  
USThis person is applicant  
for the purposes of:☐ all designated  
States☐ all designated States except  
the United States of America☒ the United States  
of America only☐ the States indicated in  
the Supplemental Box☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.**Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE**

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:

☒ agent☐ common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

GANDY, Kenneth A.  
WOODARD, EMHARDT, NAUGHTON, MORIARTY & MCNETT  
Bank One Center/Tower, Suite 3700  
111 Monument Circle  
Indianapolis, Indiana 46204 US

Telephone No.

317-634-3456

Facsimile No.

317-637-7561

Teleprinter No.

810-341-3283

SEE CONTINUATION TO BOX NO. IV ON SHEET NO. 3

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

**Box No.V DESIGNATION OF STATES**

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):

**Regional Patent**

- ☐ **AP ARIPO Patent:** GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SZ Swaziland, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☐ **EA Eurasian Patent:** AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☐ **EP European Patent:** AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☐ **OA OAPI Patent:** BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line) .....

**National Patent (if other kind of protection or treatment desired, specify on dotted line):**

- |   |   |
|---|---|
| <input type="checkbox"/> AL Albania .....                               | <input type="checkbox"/> LS Lesotho .....                                   |
| <input type="checkbox"/> AM Armenia .....                               | <input type="checkbox"/> LT Lithuania .....                                 |
| <input type="checkbox"/> AT Austria .....                               | <input type="checkbox"/> LU Luxembourg .....                                |
| <input type="checkbox"/> AU Australia .....                             | <input type="checkbox"/> LV Latvia .....                                    |
| <input type="checkbox"/> AZ Azerbaijan .....                            | <input type="checkbox"/> MD Republic of Moldova .....                       |
| <input type="checkbox"/> BA Bosnia and Herzegovina .....                | <input type="checkbox"/> MG Madagascar .....                                |
| <input type="checkbox"/> BB Barbados .....                              | <input type="checkbox"/> MK The former Yugoslav Republic of Macedonia ..... |
| <input type="checkbox"/> BG Bulgaria .....                              | <input type="checkbox"/> MN Mongolia .....                                  |
| <input type="checkbox"/> BR Brazil .....                                | <input type="checkbox"/> MW Malawi .....                                    |
| <input type="checkbox"/> BY Belarus .....                               | <input type="checkbox"/> MX Mexico .....                                    |
| <input type="checkbox"/> CA Canada .....                                | <input type="checkbox"/> NO Norway .....                                    |
| <input type="checkbox"/> CH and LI Switzerland and Liechtenstein .....  | <input type="checkbox"/> NZ New Zealand .....                               |
| <input checked="" type="checkbox"/> CN China .....                      | <input type="checkbox"/> PL Poland .....                                    |
| <input type="checkbox"/> CU Cuba .....                                  | <input type="checkbox"/> PT Portugal .....                                  |
| <input type="checkbox"/> CZ Czech Republic .....                        | <input type="checkbox"/> RO Romania .....                                   |
| <input type="checkbox"/> DE Germany .....                               | <input type="checkbox"/> RU Russian Federation .....                        |
| <input type="checkbox"/> DK Denmark .....                               | <input type="checkbox"/> SD Sudan .....                                     |
| <input type="checkbox"/> EE Estonia .....                               | <input type="checkbox"/> SE Sweden .....                                    |
| <input type="checkbox"/> ES Spain .....                                 | <input type="checkbox"/> SG Singapore .....                                 |
| <input type="checkbox"/> FI Finland .....                               | <input type="checkbox"/> SI Slovenia .....                                  |
| <input type="checkbox"/> GB United Kingdom .....                        | <input type="checkbox"/> SK Slovakia .....                                  |
| <input type="checkbox"/> GD Grenada .....                               | <input type="checkbox"/> SL Sierra Leone .....                              |
| <input type="checkbox"/> GE Georgia .....                               | <input type="checkbox"/> TJ Tajikistan .....                                |
| <input type="checkbox"/> GH Ghana .....                                 | <input type="checkbox"/> TM Turkmenistan .....                              |
| <input type="checkbox"/> GM Gambia .....                                | <input type="checkbox"/> TR Turkey .....                                    |
| <input type="checkbox"/> HR Croatia .....                               | <input type="checkbox"/> TT Trinidad and Tobago .....                       |
| <input type="checkbox"/> HU Hungary .....                               | <input type="checkbox"/> UA Ukraine .....                                   |
| <input type="checkbox"/> ID Indonesia .....                             | <input type="checkbox"/> UG Uganda .....                                    |
| <input type="checkbox"/> IL Israel .....                                | <input checked="" type="checkbox"/> US United States of America .....       |
| <input type="checkbox"/> IN India .....                                 | <input type="checkbox"/> UZ Uzbekistan .....                                |
| <input type="checkbox"/> IS Iceland .....                               | <input type="checkbox"/> VN Viet Nam .....                                  |
| <input checked="" type="checkbox"/> JP Japan .....                      | <input type="checkbox"/> YU Yugoslavia .....                                |
| <input type="checkbox"/> KE Kenya .....                                 | <input type="checkbox"/> ZW Zimbabwe .....                                  |
| <input type="checkbox"/> KG Kyrgyzstan .....                            |   |
| <input type="checkbox"/> KP Democratic People's Republic of Korea ..... |   |
| <input type="checkbox"/> KR Republic of Korea .....                     |   |
| <input type="checkbox"/> KZ Kazakhstan .....                            |   |
| <input type="checkbox"/> LC Saint Lucia .....                           |   |
| <input type="checkbox"/> LK Sri Lanka .....                             |   |
| <input type="checkbox"/> LR Liberia .....                               |   |

Check-boxes reserved for designating States (for the purposes of a national patent) which have become party to the PCT after issuance of this sheet:

- ☐ AE - United Arab Emirates .....
- ☐ ZA - South Africa .....
- ☐ .....

**Precautionary Designation Statement:** In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation of a designation consists of the filing of a notice specifying that designation and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.)

1. If, in any of the Boxes, the space is insufficient to furnish all the information: in such case, write "Continuation of Box No. ..." (indicate the number of the Box) and furnish the information in the same manner as required according to the captions of the Box in which the space was insufficient, in particular:
- (i) if more than two persons are involved as applicants and/or inventors and no "continuation sheet" is available: in such case, write "Continuation of Box No. III" and indicate for each additional person the same type of information as required in Box No. III. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below;
  - (ii) if, in Box No. II or in any of the sub-boxes of Box No. III, the indication "the States indicated in the Supplemental Box" is checked: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the applicant(s) involved and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is applicant;
  - (iii) if, in Box No. II or in any of the sub-boxes of Box No. III, the inventor or the inventor/applicant is not inventor for the purposes of all designated States or for the purposes of the United States of America: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the inventor(s) and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is inventor;
  - (iv) if, in addition to the agent(s) indicated in Box No. IV, there are further agents: in such case, write "Continuation of Box No. IV" and indicate for each further agent the same type of information as required in Box No. IV;
  - (v) if, in Box No. V, the name of any State (or OAPI) is accompanied by the indication "patent of addition," or "certificate of addition," or if, in Box No. V, the name of the United States of America is accompanied by an indication "continuation" or "continuation-in-part": in such case, write "Continuation of Box No. V" and the name of each State involved (or OAPI), and after the name of each such State (or OAPI), the number of the parent title or parent application and the date of grant of the parent title or filing of the parent application;
  - (vi) if, in Box No. VI, there are more than three earlier applications whose priority is claimed: in such case, write "Continuation of Box No. VI" and indicate for each additional earlier application the same type of information as required in Box No. VI;
  - (vii) if, in Box No. VI, the earlier application is an ARIPO application: in such case, write "Continuation of Box No. VI", specify the number of the item corresponding to that earlier application and indicate at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed.
2. If, with regard to the precautionary designation statement contained in Box No. V, the applicant wishes to exclude any State(s) from the scope of that statement: in such case, write "Designation(s) excluded from precautionary designation statement" and indicate the name or two-letter code of each State so excluded.
3. If the applicant claims, in respect of any designated Office, the benefits of provisions of the national law concerning non-prejudicial disclosures or exceptions to lack of novelty: in such case, write "Statement concerning non-prejudicial disclosures or exceptions to lack of novelty" and furnish that statement below.

## Continuation to Box No. IV Agent

WOODARD, Harold R.; EMHARDT, C. David; NAUGHTON, Joseph A., Jr.; MORIARTY, John V.; McNETT, John C.; HENRY, Thomas Q.; DURLACHER, James M.; REEVES, Charles R.; WAGNER, Vincent O.; ZLATOS, Steve; BEREVESKOS, Spiro; BAHRET, William F.; BROWNING, Clifford W.; FRISK, R. Randall; LUEDERS, Daniel J.; GANDY, Kenneth A.; THOMAS, Timothy N.; SISSELMAN, Kerry P.; JONES, Kurt N.; ALLIE, John H.; BANTA, Holiday W.; COLE, Troy J.; PAYNTER, L. Scott; LOWES, J. Andrew; MEYER, Charles J.; HARRIS, Darrin Wesley; SCHANTZ, Matthew R.; COY, Gregory B.; HIDAY, Lisa A.; DANILUCK, John V.; BROWN, Christopher A.; SCHWARTZ, Jason J.; USHER, Arthur J. IV; COLLIER, Douglas A.; MYERS, James B. Jr.; STEVENS, Scott J., and ROWE, James L., all of Woodard, Emhardt, Naughton, Moriarty & McNett, Bank One Center/Tower, Suite 3700, 111 Monument Circle, Indianapolis, Indiana 46204 United States of America

<b>Box No. VI PRIORITY CLAIM</b>		<input type="checkbox"/> Further priority claims are indicated in the Supplemental Box.		
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	national application: Regional Office	international application: receiving Office
item (1) (06.07.98) 06 July 1998	60/091,737	US		
item (2)				
item (3)				

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s): (1)

\* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.

### Box No. VII INTERNATIONAL SEARCHING AUTHORITY

**Choice of International Searching Authority (ISA)**  
(if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA / US

**Request to use results of earlier search: reference to that search** (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year) Number Country (or regional Office)  
06 July 1998 (06.07.98) 60/091,737 US

### Box No. VIII CHECK LIST: LANGUAGE OF FILING

This international application contains the following number of sheets:

request : 4  
description (excluding sequence listing part) : 16  
claims : 4  
abstract : 1  
drawings : 3  
sequence listing part of description : n/a

Total number of sheets : 28

This international application is accompanied by the item(s) marked below:

1. ☒ fee calculation sheet
2. ☐ separate signed power of attorney
3. ☐ copy of general power of attorney; reference number, if any:
4. ☐ statement explaining lack of signature
5. ☐ priority document(s) identified in Box No. VI as item(s):
6. ☐ translation of international application into (language):
7. ☐ separate indications concerning deposited microorganism or other biological material
8. ☐ nucleotide and/or amino acid sequence listing in computer readable form
9. ☒ other (specify): transmittal letter (dup)

Figure of the drawings which should accompany the abstract:

Language of filing of the international application:

English

### Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

Applicant(s):  
ELECTRON TRANSFER TECHNOLOGIES, INC.  
AYERS, William M.

Agent:

(Kenneth A. GANDY)

For receiving Office use only		2. Drawings:  <input type="checkbox"/> received:  <input type="checkbox"/> not received:
1. Date of actual receipt of the purported international application:		
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:		
4. Date of timely receipt of the required corrections under PCT Article 11(2):		
5. International Searching Authority (if two or more are competent): ISA /	6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid.	

For International Bureau use only
Date of receipt of the record copy by the International Bureau:

06 July 1999

REGARDING THE INTERNATIONAL APPLICATION OF

ELECTRON TRANSFER TECHNOLOGIES, INC., et al.

PCT OR REFERENCE NUMBER

ENTITLED

METHOD AND APPARATUS FOR THE PREPARATION OF HIGH PURITY PHOSPHINE OR OTHER GAS

Certification under 37 CFR 1.10 (if applicable)

EL016469600US

09/720663  
06 July 1999

"Express Mail" mailing number

Date of Deposit

I hereby certify that this application is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Commissioner of Patents and Trademarks, Washington, D.C. 20231.

Kenneth A. Gandy(Typed or printed name of person  
mailing application)Kenneth A. Gandy  
(Signature of person mailing  
application)

To the United States Receiving Office (RO/US):

Accompanying this transmittal letter is the above-identified International application, including a completed Request form (PCT/RO/101). Please process the application according to the provisions of the Patent Cooperation Treaty.

The following requests are made of the RO/US:

1. ☒ PREPARATION AND TRANSMITTAL OF CERTIFIED COPY OF PRIORITY DOCUMENTS—Please prepare and transmit to the International Bureau a certified copy of the United States origin priority documents identified in Box VI of the Request form (37 CFR 1.451).

To cover the cost of copy preparation and certification (37 CFR 1.19(a)(3) and (b)(1)),

☒ a (check) (money order) in the amount of \$15.00 included in fee is attached to this transmittal letter.

☐ the RO/US is hereby authorized to charge the following deposit account no.: \_\_\_\_\_

2. ☒ CHOICE OF INTERNATIONAL SEARCHING AUTHORITY—It is requested that the International Search be performed by the following International Searching Authority:

☒ United States Patent and Trademark Office (ISA/US)

☐ European Patent Office (ISA/EP)

The appropriate Search fee for the above-named Authority is indicated on the Fee Calculation Sheet (PCT/RO/101 Annex).

3. ☒ SUPPLEMENTAL SEARCH FEES (ONLY WHEN ISA/US CONDUCTS THE INTERNATIONAL SEARCH.)—Please charge any Supplemental Search fees that may be required by the United States International Searching Authority (ISA/US) to deposit account no.: 23-3030

I understand that this authorization is subject to my oral confirmation thereof in each instance and that it in no way limits my right to submit a protest against payment of the Supplemental Search fees, but is merely an administrative aid to assure that the ISA/US may timely complete the Search Report.

NOTE: SUPPLEMENTAL SEARCH FEES FOR ISA/EP ARE PAYABLE DIRECTLY TO THE EUROPEAN PATENT OFFICE

4. ☒ DISCLOSURE INFORMATION—In order to assist in screening the accompanying International application for purposes of determining whether a license for foreign transmittal should and could be granted and for other purposes, the following information is supplied:

A. ☐ There is no prior filed application relating to this invention.

B. ☒ There is a prior application, serial number 60/091,737 filed on 06 July 1998 (06.07.98) which contains subject matter that is

1. ☒ substantially identical to that of the accompanying International application.

2. ☐ less than that of the accompanying International application. The additional subject matter of the International application appears on page(s) and line(s) \_\_\_\_\_.

3. ☐ more than that of the accompanying International application.

C. ☐ Disclosure information cannot be covered by the language of Points 4A or 4B above due to the involvement of several prior applications or for other reasons. A separate sheet on which the disclosure information is explained is attached to this transmittal letter.

5. ☒ REQUEST FOR FOREIGN TRANSMITTAL LICENSE—According to the provisions of 35 U.S.C. 184 and 37 CFR 5.11, a license to transmit the accompanying International application to foreign agencies or international authorities is hereby requested.

SIGNER IS THE

☐ APPLICANT☐ COMMON REPRESENTATIVE☒ (ATTORNEY) (AGENT)

REG NO

#33,386

NAME OF SIGNER (typed)

Kenneth A. GANDY

SIGNATURE

Kenneth A. Gandy

PCT

# FEE CALCULATION SHEET

## Annex to the Request

For receiving Office use only

International application No.

Applicant's or agent's  
file reference

901713ETT

Date stamp of the receiving Office

Applicant

ELECTRON TRANSFER TECHNOLOGIES, INC., et al.

## CALCULATION OF PRESCRIBED FEES

1. TRANSMITTAL FEE . . . . . 240 T

2. SEARCH FEE . . . . . 700 S

International search to be carried out by US

(If two or more International Searching Authorities are competent in relation to the international application, indicate the name of the Authority which is chosen to carry out the international search.)

## 3. INTERNATIONAL FEE

## Basic Fee

The international application contains 28 sheets.

first 30 sheets . . . . . 455 b1

x = n/a b2

remaining sheets additional amount

Add amounts entered at b1 and b2 and enter total at B . . . . . 455 B

## Designation Fees

The international application contains 3 designations.

3 x 105 = 315 D

number of designation fees  
payable (maximum 10) amount of designation fee

Add amounts entered at B and D and enter total at I . . . . . 770 I

(Applicants from certain States are entitled to a reduction of 75% of the international fee. Where the applicant is (or all applicants are) so entitled, the total to be entered at I is 25% of the sum of the amounts entered at B and D.)

4. FEE FOR PRIORITY DOCUMENT (if applicable) . . . . . 15 P

5. TOTAL FEES PAYABLE . . . . . 1725

Add amounts entered at T, S, I and P, and enter total in the TOTAL box

TOTAL

☐ The designation fees are not paid at this time.

## MODE OF PAYMENT

☒ authorization to charge  
deposit account (see below)☐ bank draft☐ coupons☒ cheque☐ cash☐ other (specify):☐ postal money order☐ revenue stamps

## DEPOSIT ACCOUNT AUTHORIZATION (this mode of payment may not be available at all receiving Offices)

The RO/ US ☐ is hereby authorized to charge the total fees indicated above to my deposit account.☒ (this check-box may be marked only if the conditions for deposit accounts of the receiving Office so permit) is hereby authorized to charge any deficiency or credit any overpayment in the total fees indicated above to my deposit account.☐ is hereby authorized to charge the fee for preparation and transmittal of the priority document to the International Bureau of WIPO to my deposit account.

23-3030

6 July 1999

Signature Kenneth A. GANDY, U# 33, 386

Deposit Account No.

Date (day/month/year)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re PCT application of	)	Authorized Officer:
ELECTRON TRANSFER	)	Edna Wong
TECHNOLOGIES, INC.	)	
	)	
International Application	)	
Number PCT/US99/15181	)	Mailing Date
	)	27 September 2000
International Filing Date	)	
06 July 1999	)	Agent's File
	)	Reference:
Title of Invention	)	901713ETT
METHOD AND APPARATUS FOR	)	
THE PREPARATION OF HIGH PURITY	)	
PHOSPHINE OR OTHER GAS	)	

**RESPONSE TO WRITTEN OPINION**

Assistant Commissioner for Patents  
Box PCT  
Washington, D.C. 20231

Attn: IPEA/US

Dear Sir/Madam:

In response to the Written Opinion mailed 27 July 2000, regarding the above-referenced PCT Patent Application, Applicant submits substitute pages 3, 4, 10, 13, 14, and 16, to replace the corresponding original pages. Also submitted are substitute pages 17-22 to replace original pages 17-21. In these pages, certain claims have been amended, as discussed below.

Page 3 has been amended to correct the spelling of "aluminum". Page 4 has been amended to change "TE011 mode" to TE011 resonance mode". Both terms are known to those skilled in the art as shown in U.S. Patent Nos. 5,471,222 and 4,349,798, copies of which are enclosed. Page 10 has been amended to insert a generic description for "Teflon" and to correct the spelling of "including" at lines 15 and 16, respectfully. Page 13 has been amended to correct the spelling of "tantalum", and to insert a generic description for "Tefzel" (ethylene-tetrafluoro-ethylene copolymer, as indicated on the attached trade literature). Page 14 has been amended to move the extraneous "it" at line 30. Page 16 has been amended at line 24 to change "with" to "where". On page 17, claim 6 has

been amended to replace "X" with "Z" as supported by the specification at page 10, line 35. On page 18, claim 13 has been amended to change "Teflon" to "polytetrafluoroethylene". Also, claim 16 has been amended to properly claim "the precursor material" and correct the issue of antecedent basis. On page 19, claims 19 and 20, "the electrical power" has been changed to "electrical power" to correct the antecedent basis issue. New claims 32-34 have also been added to direct additional claims to preferred gas generator systems, and are set forth at new page 21. It is believed that these amendments comprehensively address the observations set forth in Section VIII of the Written Opinion.

#### **REMARKS**

Claims 1-31 remain pending, in addition to new claims 32-34. Claims 1-31 have received positive indications with regard to Novelty and Industrial Applicability. Claims 1-10, 22-24, 28 and 30-31 have received positive indications with regard to Inventive Step. The Officer is thanked for these indications. Claims 11-21, 25-27 and 29 have received negative indications with regard to Inventive Step. These indications are respectfully traversed because it is believed that claims 11-21, 25-27 and 29 do in fact possess inventive step when considered against the citations relied upon in the Written Opinion. The reasons for such belief are detailed below.

#### **I. CLAIMS 25-27 AND 29 POSSESS AN INVENTIVE STEP OVER AYERS**

The Written Opinion asserts that "Claims 25-27 and 29 lack an Inventive Step under PCT Article 33(3) as being obvious over Ayers (U.S.P. No. 5158656)." In making this assertion, the Written Opinion cites several common characteristics of the Ayers technology and the present claims. Also, however, the Written Opinion acknowledges that "Ayers does not teach a microwave transparent reaction chamber irradiated with microwave radiation." Nonetheless, the Written Opinion asserts obviousness because "it appears that the apparatus limitations in the present claims do not materially alter the overall method, absent evidence to the contrary. " It is respectfully submitted that this basis for denying an inventive step is overcome because the methods of Ayers and the present claims are entirely distinct from one another as electrochemical generation methods (Ayers) and microwave generation methods (present claims) and there is absolutely no motivation shown or explained to modify the methods of Ayers in a manner to have the present-claimed elements.



Discussing this point further, while both Ayers and the present invention may involve the production of phosphine, the apparatuses and methods by which this is achieved are entirely different. The Ayers patent expressly describes the use of an electrochemical reaction to produce the phosphine. No other modes are specified. In such a process, the rate of production is proportional to the DC current passing through the electrochemical cell. The power required is the product of the current multiplied by the cell voltage. For example, for an electrochemical phosphine generation cell operating at 200 amperes and 6 volts, with 100% current efficiency, 930 cubic centimeters per minute of phosphine would be produced. The power required would be 1200 watts ( $200 \times 6$ ) or 0.78cc/min-watt. However, the electrochemical generation approach never reaches 100% current efficiency because some of the current goes into electrochemical hydrogen production. A typical efficiency for electrochemical phosphine production is about 60%. Hence, the power efficiency is even lower ( $0.60 \times 0.78\text{cc/min-watt} = 0.47\text{ccphosphine/min-watt}$ ). Such moderated efficiencies present difficulty in semiconductor production, because phosphine must be provided at a relatively high flow rate.

On the other hand, as an illustration, with a microwave generation method, the present inventor has been able to produce 850cc/min of phosphine with only 850 watts or 1.0cc/min-watt. This is illustrated in example 1 on page 14 of the application. Consequently, this microwave generation method provided a 204% improvement in the power required to produce the phosphine over the electrochemical method of Ayers. Further, scale up of a microwave apparatus is more readily accomplished for higher flow rates than electrochemical apparatuses. High current DC power supplies are expensive and large. In addition, large bus bars or cables must be used to carry the current to the electrochemical cell. Contrasted to this, 1,000-watt microwave sources are relatively inexpensive and small. Because the microwave sources and operate with standard alternating current, they also do not require large cables like DC power supplies used in the electrochemical approach.

In view of the above remarks, it is respectfully submitted that not only is there a lack of motivation to modify the method of the Ayers patent to have the claimed elements consistent with microwave generation, but also in doing so significant improvements are enabled to facilitate the generation of high flows of produced gas. For these reasons, it is believed that Claims 25-27 and 29

possess an inventive step when considered against Ayers. Positive indication to this effect is solicited.

## **II. CLAIMS 11-21 POSSESS AN INVENTIVE STEP OVER EP 454,122**

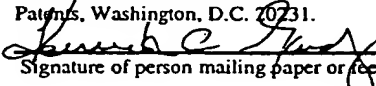
The Written Opinion asserts that "Claims 11-21 lack an inventive step under PCT Article 33(3) as being obvious over EP 454,122." In making this assertion, the Written Opinion observes several elements of the present claimed invention that are present in the disclosure of EP 454,122. In one aspect, the Written Opinion asserts that EP 454,122 teaches "a microwave transparent, gas-type barrier 3". However, the references teaches no such barrier. Instead, in the EP reference, the element (3) is defined as "a closed apparatus body". In particular, on page 8, lines 20 and 38 and in figures 6, 7 and 8, the microwave source is connected to the closed apparatus body through a "waveguide". This waveguide does not contain a microwave transparent window material. Instead, waveguides are generally understood to include hollow metallic pipes or pipes with rectangular cross-section. Thus, as disclosed the EP device is devoid of any microwave transparent barrier as provided in the present claims. In order to clarify the use of the microwave transparent, gas-tight barrier in the instant claims, Claim 11 has been amended to specify that the "microwave radiation is directed through said microwave transparent, gas-tight barrier." This is contrary to the teachings of the EP reference. In addition, this is highly important in the generation of phosphine or similar corrosive gases. In the absence of such a gas-tight barrier, one risks corrosion of the microwave source by the corrosive gases. Further, in the absence of such a gas-tight barrier, one cannot pressurize the reaction as is desirable in the generation of phosphine and other similar gases.

For these reasons, it is submitted that Claims 1-21 possess an inventive step in reference to the reactor disclosed in EP 454,122. Reconsideration of the issue of inventive step and a positive indication in this regard are solicited.

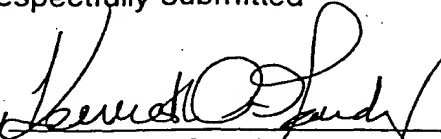
New claims 32-34 have been added and are directed to a gas generation system. Support for the recited elements can be found, for example, in the Summary of the Invention. Favorable consideration of these claims is also solicited.

A second copy of the Written Opinion was mailed by the Office on September 12, 2000. Because the two copies are perceived to be the same, it is believed that this response is sufficient to reply to both Written Opinions. The Officer is requested to telephone the undersigned attorney if that is not the case.

In view of the foregoing, it is submitted that the International Preliminary Examination Report should be positive in all respects in regard to all claims.  
Action to that end is solicited.

<p>"Express Mail" label number <u>EL41447861US</u> Date of Deposit <u>Sept. 27, 2000</u> I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR §1.10 on the date indicated above and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.  Signature of person mailing paper or fee</p>
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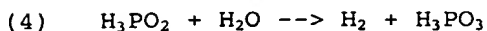
Respectfully submitted

By   
Kenneth A. Gandy, #33,386  
Woodard, Emhardt, Naughton,  
Moriarty & McNett  
Bank One Center/Tower, Suite 3700  
111 Monument Circle  
Indianapolis, Indiana 46204 US  
(317) 634-3456



A side reaction which is catalyzed by metals is

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10 H.J. Banks and C.J. Waterford, U.S. Pat. No. 5,573,740, disclose a chemical method for generating phosphine based on the reaction of water or water vapor with a metal phosphide. W.Frierel and R. Ehert, U.S. Pat. No. 4,720,380 disclose an aluminum phosphide formulation for generation of phosphine for pesticidal applications. Both methods produce a dilute, moist phosphine for use as a pesticidal gas. This low concentration, impure gas is unsuitable for semiconductor applications.

20 C.R. Strauss and A.F. Faux, U.S. Pat. No. 5,387,397, disclose a method and apparatus for chemical reactions based on feeding reactants through a microwave-heated zone. This method is only appropriate for liquid phase or liquid slurry reactions in which the product is a liquid. No provision is made for phase change and gas product production and expansion within the reaction zone. Furthermore, Strauss's specification of a small diameter coiled tube in the microwave-heated region precludes refluxing of the chemical reaction in the heated region and hence limits the product yield.

30 Koch, in U.S. Patent No. 5,529,669 teaches the use of single mode microwave radiation to raise the temperature of a metal catalyst and thereby increase the reaction rate between ammonia and a hydrocarbon containing gas. Koch feeds two gas phase reactants over a microwave-heated catalyst. The product of the gas phase reaction is another gas, hydrogen cyanide. No phase change or allowances for phase change is taught in their patent. Furthermore no allowances are made for refluxing of reactants to increase the reaction yield of the products.

T. A. Koch, K.R. Krause, and M. Mehdizadeh (U.S. Pat. Nos. 5,470,541 and 5,529,669) disclose a process for the preparation of hydrogen cyanide. Their method specifies a tubular reactor within a resonant cavity tuned to the TE011 resonance mode of a microwave source.

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One major limitation of these inventions is the use of one material (Teflon or glass) as the conduit for exposing the reactants to microwave energy. This limits the type of reactions which can be carried out. Teflon is limited to temperature below 260° C and glass or quartz is attacked and corroded by hot alkali and some acid solutions.

10

Description Of The Preferred Embodiments

For the purposes of promoting an understanding of the principles of the invention, reference will now be made to  
5   embodiments thereof and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations, further modifications and applications of the principles of the invention as described herein being contemplated as would normally  
10   occur to one skilled in the art to which the invention pertains.

Referring now to FIG. 1, shown is a preferred reactor system of the invention. The reactor includes a reaction chamber tube 1 of a microwave transparent material (e.g. fused silica, silicon dioxide,  
15   boron nitride, graphite or Teflon (polytetrafluoroethylene)) that is irradiated with microwave radiation from a radiation source including a magnetron 2 attached to a waveguide 3. This microwave radiation source may, for example, have a frequency of about 0.9 GHz or from about 2.41 to about 10 GHz. The reaction chamber 1 is contained  
20   within a microwave reflecting enclosure 4, for instance constructed of an electrically conductive material desirably having a conductivity of at least about  $10^{-3}$  ohm/cm. The enclosure 4 also preferably has a smallest dimension at least twice the wavelength of the microwave radiation to be employed. At the bottom of the reaction chamber 1 is  
25   a high boiling point liquid (HBPL) such as phosphoric acid or silicon oil which absorbs the microwave radiation.

A pump 5 transports a precursor material, preferably a liquid, from a feed source 6 into the reaction chamber 1 at a fixed or variable, preferably fixed, feed rate. The precursor material is  
30   capable of reacting in the reaction chamber 1 to produce a desired gas. In the production of phosphine, the precursor material may for example be an aqueous solution of  $H_3PO_2$ , an aqueous solution of  $H_3PO_3$ , an aqueous solution of a salt of the formula  $XH_2PO_2$  or  $XH_2PO_3$  wherein X is an alkali metal such as Li, Na or K, an aqueous solution of a salt  
35   of the formula  $Z_2(H_2PO_2)_2$  wherein Z is an alkaline earth metal such as Ca, Mg, Sr, or Ba, or an alkaline (e.g. aqueous NaOH, KOH or LiOH)

to the metal plate with an O-ring or other pressure-tight seal to prevent gas from escaping around the window 22. A wave guide 23 and one or more magnetrons 24 are mounted on the waveguide. Microwave radiation from the magnetron is directed through the microwave transparent window into the fluid 25 held in the reaction chamber.

The window can be made thicker and have a smaller area than the microwave transparent tube shown in Fig. 1. Both of these factors allow the window to withstand higher pressures than the tube configuration. By this means the temperature and pressure limitations of materials currently used in microwave transparent tubes or conduits in the reaction chamber are overcome. This allows higher pressure gas product to be produced with less concern of materials failure and gas leakage from the reactor. The inside of the reaction chamber can also be coated with a corrosion-resistant coating (e.g. tantalum or Tefzel ethylene-tetrafluoroethylene copolymer), to eliminate contact of the hot fluid with the chamber walls.

In yet another preferred embodiment of the invention, Fig. 3 illustrates a microwave transparent reflux tube 31 extending partway up the height of a stainless steel vessel 32. Holes in the bottom of the reflux tube allow the HBPL to flow into a concentric outer container 33 thereby controlling the liquid height in the reflux tube. Reaction product phosphoric acid liquid overflows the edge of the outer container and exits the steel vessel through a drain 34. The reactant feed liquid is fed into the center tube 31 where it contacts the hot HBPL and flash evaporates. The reactant liquid and vapor reflux within the center tube until the reaction reaches completion. The product gas exits the steel chamber through a port 35.

It will be understood that the reactor systems illustrated in Figs. 2 and 3 can be equipped with similar manifold and control features to those illustrated in Fig. 1. Thus, the systems of Figs. 2 and 3 can include components corresponding to those numbered 7-15 in Fig. 1.

The following examples illustrate, but do not define or limit, the invention.

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EXAMPLE 1

One particular configuration for the process for producing phosphine is the thermal decomposition of  $\text{H}_3\text{PO}_2$ . Phosphine was generated using a vertical tubular reactor made of Teflon-PFA. The reactor had an inside diameter of 0.957 inch, outside diameter of 1.315 inch and total length of 35 inches. The reactor consists of three zones; an entrance zone (of length 8.5 inches), a microwave irradiated reaction and reflux zone (of length 10 inches) and an overflow zone (of length 16.5 inches). The extended zones of entrance and overflow were used to assist reactant reflux, cooling, and gas-liquid separation of the hot reaction products before they reach the exit port. The microwave transparent tube was irradiated with approximately 850 watts at 2.45 Ghz.

The phosphine was generated at  $240^\circ\text{C}$  and 25 pounds per square inch outlet pressure. The rate of phosphine gas production proportional to microwave wattage heating the reaction zone. The liquid feed, 50%  $\text{H}_3\text{PO}_2$  in water, was pumped into the bottom of the tube at 2.6 and 10.8 milliliters/min. At the liquid feed rate of 2.6ml/min the conversion of  $\text{H}_3\text{PO}_2$  to  $\text{PH}_3$  was 94 % with a phosphine production rate of 260 standard cubic centimeter per minutes (sccm). At a feed rate of 10.8 ml/min the conversion was 73 % with a phosphine production rate of 850 sccm. In both cases, the purity of the phosphine was greater than 99.99%.

During microwave heating of the liquid, about 75% of the reactor volume is filled with a two-phase gas liquid foam consisting of phosphorous acids, water vapor, and phosphine. The two-phase foam refluxes in the reaction zone until some of it overflows out of the phosphine exit port on the tube. At the end of the production run, the solution remaining in the reactor tube consists over 90%  $\text{H}_3\text{PO}_4$  in water. This solution is used as the high boiling point liquid heating medium.



at 85° C. Faster production rates of phosphine can be produced at higher temperatures up to the material limits of the reaction zone material.

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EXAMPLE 3

In a modification of the process, some applications for semiconductor growth may require a different phosphine concentration than produced by the generator. With conventional gas cylinders, different gas concentrations would have to be pre-mixed to the desired concentration before filling the gas cylinder. In a modification of the phosphine generator, a feedback loop is used to control the mixing of the two gases and thereby maintain the desired gas concentration. This makes phosphine generator more versatile in that it can provide a wide range of gas concentrations.

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The operator of the phosphine generator desires to provide 50% phosphine in hydrogen to the CVD deposition reactor. The operator selects this desired concentration from the software program. The microprocessor then determines the concentration of phosphine flowing through a concentration sensor. The computer program compares this concentration to the set point or desired concentration. A mass flow controller (MFC) then allows a diluting gas, hydrogen, to flow into a mixing tee where it is completely mixed with the phosphine.

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The mixed gas then enters the concentration monitor where the mixed final concentration is determined. The MFC is then directed by the PC program to increase or decrease the diluent flow to maintain the set point concentration value. By this means, the operator can set and control any concentration between 0% and the maximum phosphine concentration produced by the generator.

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I claim:

1. A method of generating high purity phosphine gas, comprising producing phosphine gas by the interaction of microwave radiation with a precursor material while said precursor material  
5 passes through a microwave transparent, metal free, gas impermeable, pressurized reaction zone.
2. The method of Claim 1 wherein the precursor material is  $H_3PO_2$  in an aqueous solution.  
10
3. The method of Claim 1 wherein the precursor material is  $H_3PO_3$  in an aqueous solution .
4. The method of Claim 1 wherein the precursor material is  
15 crystalline  $H_3PO_2$  or crystalline  $H_3PO_3$ .
5. The method of Claim 1 wherein the precursor material is a salt of the formula  $XH_2PO_2$  in an aqueous solution where X is selected from the alkali metals group consisting of Li, Na, and K.  
20
6. The method of Claim 1 wherein the precursor material is a salt of the formula  $Z_2(H_2PO_2)_2$  in an aqueous solution where Z is selected from the alkaline metals group consisting of Ca, Mg, Sr, and Ba.  
25
7. The method of Claim 1 wherein the precursor material is a salt of the formula  $XH_2PO_3$  in an aqueous solution where X is selected from the alkali metals group consisting of Li, Na, and K.
8. The method of Claim 1 wherein the precursor material is a  
30 slurry of red phosphorus in an alkaline solution.
9. The method of Claim 8 wherein the alkaline solution is selected from the group consisting of NaOH, KOH, and LiOH dissolved in  
35 water or combinations thereof.
10. The method of Claim 1 wherein the high purity gas contains no more than 100 parts per million of oxygen or water vapor.

11. A chemical reactor system for generation of high purity gas, comprised of a source of microwave radiation, a microwave transparent, gas tight barrier through which said source of microwave radiation is directed, a microwave reflecting enclosure into which said source of microwave radiation is directed, a manifold for gas delivery adapted to receive generated gas from said enclosure, a solvent vapor removal device adapted to remove solvent vapor from the generated gas, a gas concentration sensor for sensing gas concentration in the generated gas, and a feed-back control system to control gas generation rate in said enclosure.

12. The system of Claim 11, wherein the microwave radiation source has a frequency of 0.9 GHz, or 2.41 to 10 GHz.

13. The system of Claim 11, wherein the microwave transparent barrier is constructed from materials chosen from the group polytetrafluoroethylene, fused silica, silicon dioxide, boron nitride, or graphite.

14. The system of Claim 11, wherein the microwave reflecting enclosure is constructed from an electrically conductive material with a conductivity of a least  $10^{-3}$  ohm/cm.

15. The system of Claim 11, wherein the microwave reflecting enclosure has a smallest dimension of at least twice the wavelength of the microwave radiation.

16. The system of Claim 11, also comprising a precursor material for generating said gas, and wherein the precursor material is selected from the group consisting of hypophosphorous acid, hypophoric acid, and an alkaline slurry of red phosphorous.

17. The system of Claim 11 wherein the vapor removal device contains silica gel.

18. The system of Claim 11, wherein the feedback control system includes a microprocessor controlled temperature feedback loop

to a raw material feed pump, and microwave radiation source power supply.

5 19. The system of Claim 11 wherein the feedback control system modulates electrical power to the microwave radiation source to maintain a constant gas delivery pressure.

10 20. The system of Claim 11 wherein the feedback control system modulates electrical power to the microwave radiation source to provide a variable gas flow rate.

15 21. The system of Claim 11 wherein the feedback control system modulates the microwave radiation frequency to control the reaction product selectivity.

22. A concentration control system for phosphine product gas, comprising:

a concentration monitor for measuring the ratio of phosphine to diluting gas in a product gas stream;

20 a microprocessor based comparator to determine the present concentration versus a desired concentration of phosphine gas in the product gas stream; and

25 a gas flow controller to control the introduction of a diluting gas into the product gas stream in response to a signal generated based on said determination.

30 23. The system of claim 22, wherein the phosphine gas is generated by reaction of a precursor material under the influence of microwave radiation.

35 24. A method for generating a high purity gas for semiconductor processing, comprising producing the gas by the interaction of microwave radiation with a precursor material while said precursor material passes through a microwave transparent, metal free, gas impermeable, pressurized reaction zone.

25. A method for fabricating a semiconductor device using a gas, characterized by the use of the gas when produced by the reaction of a precursor material under the influence of microwave radiation.

5           26. The method of claim 25, which comprises:  
            producing the gas continuously by a continuous introduction and  
            reaction of the precursor material in a microwave transparent reaction  
            chamber irradiated with microwave radiation; and  
10           feeding the produced gas continuously as it is formed to a  
            semiconductor fabrication process.

            27. The method of claim 26, wherein the gas is continuously  
            fed as it is produced to a chemical vapor deposition reactor or an  
            oxidation furnace.

15           28. The method of any of claims 24-27, wherein the precursor  
            material is liquid, and wherein the reaction produces a two-phase  
            system including the gas.

20           29. The method of any of claims 24-28, wherein the gas is  
            phosphine.

            30. An apparatus for the fabrication of a semiconductor  
            device, comprising:  
25           a gas generation reactor for generating a gas, the gas  
            generation reactor having a microwave transparent reaction chamber and  
            a source of microwave radiation directed into the reaction chamber;  
            and  
            a chemical vapor deposition reactor or an oxidation furnace  
30           coupled to the gas generation reactor.

            31. The apparatus of claim 30, wherein the gas is phosphine.

            32. A chemical reactor system for generation of high purity  
35           gas for semiconductor fabrication, comprised of:  
            a source of microwave radiation;

a reaction chamber for receiving a precursor material for generating said gas, said reaction chamber adapted to generate said gas under pressure;

5 a microwave transparent, gas tight barrier through which said source of microwave radiation is directed into said reaction chamber;

a microwave reflecting enclosure into which said source of microwave radiation is directed;

a manifold for gas delivery adapted to receive the generated gas; and

10 a solvent vapor removal device adapted to remove solvent vapor from the generated gas.

33. The system of claim 32, also comprising a supply of precursor material coupled to said reaction chamber.

15

34. The system of claim 33, also comprising:

a gas concentration sensor for sensing gas concentration in the generated gas; and

20 a feed-back control system to control gas generation rate in said reaction chamber.

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Abstract

5 A chemical apparatus and method for the generation of high  
purity phosphine gas or another gas used in the production and doping  
of semiconductors is described. The preferred apparatus includes a  
means for generating the gas with microwave radiation, a means for  
controlling the production rate, means for purifying the product gas,  
and a means for controlled blending of the gas with a diluent gas to a  
10 desired delivery composition. By these means, gas of sufficient  
purity, at the proper pressure, and in the required volume, is  
generated for direct introduction into a process in which  
semiconductors are manufactured and doped.

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PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

REC'D 07 FEB 2001

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Applicant's or agent's file reference 901713ETT	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US99/15181	International filing date (day/month/year) 06 JULY 1999	Priority date (day/month/year) 06 JULY 1998
International Patent Classification (IPC) or national classification and IPC Please See Supplemental Sheet.		
Applicant ELECTRON TRANSFER TECHNOLOGIES, INC.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This ~~REPORT~~ consists of a total of 6 sheets.  
☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority. (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 11 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of report with regard to novelty, inventive step or industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☒ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand  01 FEBRUARY 2000	Date of completion of this report  30 SEPTEMBER 2000
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer <u>B. H. Wong</u> EDNA WONG
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0661

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## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US99/15181

## I. Basis of the report

## 1. With regard to the elements of the international application:\*

☐ the international application as originally filed☒ the description:

pages (See Attached) \_\_\_\_\_, as originally filed

pages \_\_\_\_\_, filed with the demand

pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

☒ the claims:

pages (See Attached) \_\_\_\_\_, as originally filed

pages \_\_\_\_\_, as amended (together with any statement) under Article 19

pages \_\_\_\_\_, filed with the demand

pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

☒ the drawings:

pages (See Attached) \_\_\_\_\_, as originally filed

pages \_\_\_\_\_, filed with the demand

pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

☒ the sequence listing part of the description:

pages (See Attached) \_\_\_\_\_, as originally filed

pages \_\_\_\_\_, filed with the demand

pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

## 2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language \_\_\_\_\_ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).☐ the language of publication of the international application (under Rule 48.3(b)).☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

## 3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

☐ contained in the international application in printed form.☐ filed together with the international application in computer readable form.☐ furnished subsequently to this Authority in written form.☐ furnished subsequently to this Authority in computer readable form.☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.4. ☒ The amendments have resulted in the cancellation of:☒ the description, pages NONE☒ the claims, Nos. NONE☒ the drawings, sheets/fig NONE5. ☒ This report has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).\*\*

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

\*\*Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

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## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US99/15181

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement****1. statement**

Novelty (N)	Claims <u>1-34</u>	YES
	Claims <u>NONE</u>	NO
Inventive Step (IS)	Claims <u>1-34</u>	YES
	Claims <u>NONE</u>	NO
Industrial Applicability (IA)	Claims <u>1-34</u>	YES
	Claims <u>NONE</u>	NO

**2. citations and explanations (Rule 70.7)**

Claims 1-34 meet novelty under PCT Article 33(2) as not being anticipated by the prior art of record.

Claims 1-34 meet an inventive step under PCT Article 33(3) as not being obvious over the prior art of record.

Claims 1-34 meet the criteria set out in PCT Article 33(4) because a high purity gas is generated for the fabrication of a semiconductor device.

----- NEW CITATIONS -----  
NONE

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# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US99/15181

## VI. Certain documents cited

### 1. Certain published documents (Rule 70.10)

<u>Application No. Patent No.</u>	<u>Publication Date (day/month/year)</u>	<u>Filing Date (day/month/year)</u>	<u>Priority date (valid claim) (day/month/year)</u>
US, A, 5,951,831	14 SEPTEMBER 1999	11 JULY 1997	

### 2. Non-written disclosures (Rule 70.9)

<u>Kind of non-written disclosure</u>	<u>Date of non-written disclosure (day/month/year)</u>	<u>Date of written disclosure referring to non-written disclosure (day/month/year)</u>

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US99/15181

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

Claim 34 is objected to under PCT Rule 66.2(a)(v) as lacking clarity under PCT Article 6 because the claim is indefinite for the following reason(s):

line 5, the original specification and original claim 11, lines 9-10, recite that the "feed-back control system to control gas generation rate in said enclosure". There is no support for "a feed-back control system to control gas generation rate in said reaction chamber".

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## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US99/15181

**Supplemental Box**

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

Sheet 10

**CLASSIFICATION:**

The International Patent Classification (IPC) and/or the National classification are as listed below:

IPC(7): C01B 53/00; H05B 6/50; A61L 2/00; A47J 37/08; C23C 16/00 and US Cl.: 204/157.43; 219/707; 422/21; 96/397; 438/800, 935; 118/715

**I. BASIS OF REPORT:**

This report has been drawn on the basis of the description,

page(s) 1-2,5-9,11-12,15, as originally filed.

page(s) NONE, filed with the demand.

and additional amendments:

Pages 4,10,13-14,16, filed with the letter of 29 September 2000.

Page 3, filed with the letter of 02 October 2000.

This report has been drawn on the basis of the claims,

page(s) NONE, as originally filed.

page(s) NONE, as amended under Article 19.

page(s) NONE, filed with the demand.

and additional amendments:

Pages 17-21, filed with the letter of 29 September 2000.

This report has been drawn on the basis of the drawings,

page(s) 1-3, as originally filed.

page(s) NONE, filed with the demand.

and additional amendments:

NONE

This report has been drawn on the basis of the sequence listing part of the description:

page(s) NONE, as originally filed.

pages(s) NONE, filed with the demand.

and additional amendments:

NONE

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PCT/US 99/1518

IPEA/US 02 OCT 2000

- 3 -



A side reaction which is catalyzed by metals is

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10 H.J. Banks and C.J. Waterford, U.S. Pat. No. 5,573,740, disclose a chemical method for generating phosphine based on the reaction of water or water vapor with a metal phosphide. W.Frierel and R. Ehert, U.S. Pat. No. 4,720,380 disclose an aluminum phosphide formulation for generation of phosphine for pesticidal applications. Both methods produce a dilute, moist phosphine for use as a pesticidal gas. This 15 low concentration, impure gas is unsuitable for semiconductor applications.

20 C.R. Strauss and A.F. Faux, U.S. Pat. No. 5,387,397, disclose a method and apparatus for chemical reactions based on feeding reactants through a microwave-heated zone. This method is only appropriate for liquid phase or liquid slurry reactions in which the product is a liquid. No provision is made for phase change and gas product production and expansion within the reaction zone. Furthermore, Strauss's specification of a small diameter coiled tube in the 25 microwave-heated region precludes refluxing of the chemical reaction in the heated region and hence limits the product yield.

30 Koch, in U.S. Patent No. 5,529,669 teaches the use of single mode microwave radiation to raise the temperature of a metal catalyst and thereby increase the reaction rate between ammonia and a hydrocarbon containing gas. Koch feeds two gas phase reactants over a microwave-heated catalyst. The product of the gas phase reaction is another gas, hydrogen cyanide. No phase change or allowances for phase change is taught in their patent. Furthermore no allowances are 35 made for refluxing of reactants to increase the reaction yield of the products.

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PCT/US 99/15181  
IPEA/US 29 SEP 2000

- 4 -

T. A. Koch, R.R. Krause, and M. Mehdizadeh (U.S. Pat. Nos. 5,470,541 and 5,529,669) disclose a process for the preparation of hydrogen cyanide. Their method specifies a tubular reactor within a resonant cavity tuned to the TE011 resonance mode of a microwave source.

5

One major limitation of these inventions is the use of one material (Teflon or glass) as the conduit for exposing the reactants to microwave energy. This limits the type of reactions which can be carried out. Teflon is limited to temperature below 260° C and glass or quartz is attacked and corroded by hot alkali and some acid solutions.

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PCT/US 99/15181

IPEA/US 29 SEP 2000

- 10 -

Description Of The Preferred Embodiments

For the purposes of promoting an understanding of the principles of the invention, reference will now be made to  
5 embodiments thereof and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations,  
further modifications and applications of the principles of the invention as described herein being contemplated as would normally  
10 occur to one skilled in the art to which the invention pertains.

Referring now to FIG. 1, shown is a preferred reactor system of the invention. The reactor includes a reaction chamber tube 1 of a  
15 microwave transparent material (e.g. fused silica, silicon dioxide, boron nitride, graphite or Teflon (polytetrafluoroethylene)) that is irradiated with microwave radiation from a radiation source including  
a magnetron 2 attached to a waveguide 3. This microwave radiation source may, for example, have a frequency of about 0.9 GHz or from  
about 2.41 to about 10 GHz. The reaction chamber 1 is contained  
20 within a microwave reflecting enclosure 4, for instance constructed of an electrically conductive material desirably having a conductivity of at least about  $10^{-1}$  ohm/cm. The enclosure 4 also preferably has a  
smallest dimension at least twice the wavelength of the microwave radiation to be employed. At the bottom of the reaction chamber 1 is  
25 a high boiling point liquid (HBPL) such as phosphoric acid or silicon oil which absorbs the microwave radiation.

A pump 5 transports a precursor material, preferably a liquid, from a feed source 6 into the reaction chamber 1 at a fixed or  
variable, preferably fixed, feed rate. The precursor material is  
30 capable of reacting in the reaction chamber 1 to produce a desired gas. In the production of phosphine, the precursor material may for example be an aqueous solution of  $H_3PO_2$ , an aqueous solution of  $H_3PO_3$ ,  
an aqueous solution of a salt of the formula  $XH_2PO_2$  or  $XH_2PO_3$  wherein X is an alkali metal such as Li, Na or K, an aqueous solution of a salt  
35 of the formula  $Z_2(H_2PO_2)_2$  wherein Z is an alkaline earth metal such as Ca, Mg, Sr, or Ba, or an alkaline (e.g. aqueous NaOH, KOH or LiOH)

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PCT/US 99/15181

IPEA/US 29 SEP 2000

- 13 -

to the metal plate with an O-ring or other pressure-tight seal to prevent gas from escaping around the window 22. A wave guide 23 and one or more magnetrons 24 are mounted on the waveguide. Microwave radiation from the magnetron is directed through the microwave transparent window into the fluid 25 held in the reaction chamber.

The window can be made thicker and have a smaller area than the microwave transparent tube shown in Fig. 1. Both of these factors allow the window to withstand higher pressures than the tube configuration. By this means the temperature and pressure limitations of materials currently used in microwave transparent tubes or conduits in the reaction chamber are overcome. This allows higher pressure gas product to be produced with less concern of materials failure and gas leakage from the reactor. The inside of the reaction chamber can also be coated with a corrosion-resistant coating (e.g. tantalum or Tefzel ethylene-tetrafluoroethylene copolymer), to eliminate contact of the hot fluid with the chamber walls.

In yet another preferred embodiment of the invention, Fig. 3 illustrates a microwave transparent reflux tube 31 extending partway up the height of a stainless steel vessel 32. Holes in the bottom of the reflux tube allow the HBPL to flow into a concentric outer container 33 thereby controlling the liquid height in the reflux tube. Reaction product phosphoric acid liquid overflows the edge of the outer container and exits the steel vessel through a drain 34. The reactant feed liquid is fed into the center tube 31 where it contacts the hot HBPL and flash evaporates. The reactant liquid and vapor reflux within the center tube until the reaction reaches completion. The product gas exits the steel chamber through a port 35.

It will be understood that the reactor systems illustrated in Figs. 2 and 3 can be equipped with similar manifold and control features to those illustrated in Fig. 1. Thus, the systems of Figs. 2 and 3 can include components corresponding to those numbered 7-15 in Fig. 1.

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PCTAUS 99/15181

IPEA/US 29 SEP 2000

- 14 -

The following examples illustrate, but do not define or limit, the invention.

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EXAMPLE 1

One particular configuration for the process for producing phosphine is the thermal decomposition of  $H_3PO_2$ . Phosphine was generated using a vertical tubular reactor made of Teflon-PFA. The reactor had an inside diameter of 0.957 inch, outside diameter of 1.315 inch and total length of 35 inches. The reactor consists of three zones; an entrance zone (of length 8.5 inches), a microwave irradiated reaction and reflux zone (of length 10 inches) and an overflow zone (of length 16.5 inches). The extended zones of entrance and overflow were used to assist reactant reflux, cooling, and gas-liquid separation of the hot reaction products before they reach the exit port. The microwave transparent tube was irradiated with approximately 850 watts at 2.45 Ghz.

The phosphine was generated at 240°C and 25 pounds per square inch outlet pressure. The rate of phosphine gas production proportional to microwave wattage heating the reaction zone. The liquid feed, 50%  $H_3PO_2$  in water, was pumped into the bottom of the tube at 2.6 and 10.8 milliliters/min. At the liquid feed rate of 2.6ml/min the conversion of  $H_3PO_2$  to  $PH_3$  was 94 % with a phosphine production rate of 260 standard cubic centimeter per minutes (scm). At a feed rate of 10.8 ml/min the conversion was 73 % with a phosphine production rate of 850 scm. In both cases, the purity of the phosphine was greater than 99.99%.

During microwave heating of the liquid, about 75% of the reactor volume is filled with a two-phase gas liquid foam consisting of phosphorous acids, water vapor, and phosphine. The two-phase foam refluxes in the reaction zone until some of it overflows out of the phosphine exit port on the tube. At the end of the production run, the solution remaining in the reactor tube consists over 90%  $H_3PO_2$  in water. This solution is used as the high boiling point liquid heating medium.

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PCTAUS 99/15181

IPEAUS 29 SEP 2000

- 16 -

at 85° C. Faster production rates of phosphine can be produced at higher temperatures up to the material limits of the reaction zone material.

5

EXAMPLE 3

In a modification of the process, some applications for semiconductor growth may require a different phosphine concentration than produced by the generator. With conventional gas cylinders, different gas concentrations would have to be pre-mixed to the desired concentration before filling the gas cylinder. In a modification of the phosphine generator, a feedback loop is used to control the mixing of the two gases and thereby maintain the desired gas concentration. This makes phosphine generator more versatile in that it can provide a wide range of gas concentrations.

15

The operator of the phosphine generator desires to provide 50% phosphine in hydrogen to the CVD deposition reactor. The operator selects this desired concentration from the software program. The microprocessor then determines the concentration of phosphine flowing through a concentration sensor. The computer program compares this concentration to the set point or desired concentration. A mass flow controller (MFC) then allows a diluting gas, hydrogen, to flow into a mixing tee where it is completely mixed with the phosphine.

20

The mixed gas then enters the concentration monitor where the mixed final concentration is determined. The MFC is then directed by the PC program to increase or decrease the diluent flow to maintain the set point concentration value. By this means, the operator can set and control any concentration between 0% and the maximum phosphine concentration produced by the generator.

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PCT/US 99/15181

IPEA/US 29 SEP 2000

- 17 -

I claim:

1. A method of generating high purity phosphine gas, comprising producing phosphine gas by the interaction of microwave radiation with a precursor material while said precursor material passes through a microwave transparent, metal free, gas impermeable, pressurized reaction zone.
2. The method of Claim 1 wherein the precursor material is  $H_3PO_2$  in an aqueous solution.
3. The method of Claim 1 wherein the precursor material is  $H_3PO_2$  in an aqueous solution.
4. The method of Claim 1 wherein the precursor material is crystalline  $H_3PO_2$  or crystalline  $H_3PO_3$ .
5. The method of Claim 1 wherein the precursor material is a salt of the formula  $XH_2PO_2$  in an aqueous solution where X is selected from the alkali metals group consisting of Li, Na, and K.
6. The method of Claim 1 wherein the precursor material is a salt of the formula  $Z_2(H_2PO_2)_2$  in an aqueous solution where Z is selected from the alkaline metals group consisting of Ca, Mg, Sr, and Ba.
7. The method of Claim 1 wherein the precursor material is a salt of the formula  $XH_2PO_3$  in an aqueous solution where X is selected from the alkali metals group consisting of Li, Na, and K.
8. The method of Claim 1 wherein the precursor material is a slurry of red phosphorus in an alkaline solution.
9. The method of Claim 8 wherein the alkaline solution is selected from the group consisting of NaOH, KOH, and LiOH dissolved in water or combinations thereof.
10. The method of Claim 1 wherein the high purity gas contains no more than 100 parts per million of oxygen or water vapor.

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PCT/US 99/15181

- 18 -

IPEA/US 29 SEP 2000

11. A chemical reactor system for generation of high purity gas, comprised of a source of microwave radiation, a microwave transparent, gas tight barrier through which said source of microwave radiation is directed, a microwave reflecting enclosure into which said source of microwave radiation is directed, a manifold for gas delivery adapted to receive generated gas from said enclosure, a solvent vapor removal device adapted to remove solvent vapor from the generated gas, a gas concentration sensor for sensing gas concentration in the generated gas, and a feed-back control system to control gas generation rate in said enclosure.

12. The system of Claim 11, wherein the microwave radiation source has a frequency of 0.9 GHz, or 2.41 to 10 GHz.

13. The system of Claim 11, wherein the microwave transparent barrier is constructed from materials chosen from the group polytetrafluoroethylene, fused silica, silicon dioxide, boron nitride, or graphite.

14. The system of Claim 11, wherein the microwave reflecting enclosure is constructed from an electrically conductive material with a conductivity of a least  $10^{-1}$  ohm/cm.

15. The system of Claim 11, wherein the microwave reflecting enclosure has a smallest dimension of at least twice the wavelength of the microwave radiation.

16. The system of Claim 11, also comprising a precursor material for generating said gas, and wherein the precursor material is selected from the group consisting of hypophosphorous acid, hypophoric acid, and an alkaline slurry of red phosphorous.

17. The system of Claim 11 wherein the vapor removal device contains silica gel.

18. The system of Claim 11, wherein the feedback control system includes a microprocessor controlled temperature feedback loop

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PCT/US 99/15181  
IPEA/US 29 SEP 2000

- 19 -

to a raw material feed pump, and microwave radiation source power supply.

5 19. The system of Claim 11 wherein the feedback control system modulates electrical power to the microwave radiation source to maintain a constant gas delivery pressure.

10 20. The system of Claim 11 wherein the feedback control system modulates electrical power to the microwave radiation source to provide a variable gas flow rate.

15 21. The system of Claim 11 wherein the feedback control system modulates the microwave radiation frequency to control the reaction product selectivity.

22. A concentration control system for phosphine product gas, comprising:

a concentration monitor for measuring the ratio of phosphine to diluting gas in a product gas stream;

20 a microprocessor based comparator to determine the present concentration versus a desired concentration of phosphine gas in the product gas stream; and

25 a gas flow controller to control the introduction of a diluting gas into the product gas stream in response to a signal generated based on said determination.

30 23. The system of claim 22, wherein the phosphine gas is generated by reaction of a precursor material under the influence of microwave radiation.

35 24. A method for generating a high purity gas for semiconductor processing, comprising producing the gas by the interaction of microwave radiation with a precursor material while said precursor material passes through a microwave transparent, metal free, gas impermeable, pressurized reaction zone.

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PCT/US 99/15181

IPEA/US 29 SEP 2000

- 20 -

25. A method for fabricating a semiconductor device using a gas, characterized by the use of the gas when produced by the reaction of a precursor material under the influence of microwave radiation.

5           26. The method of claim 25, which comprises:  
            producing the gas continuously by a continuous introduction and  
            reaction of the precursor material in a microwave transparent reaction  
            chamber irradiated with microwave radiation; and  
            feeding the produced gas continuously as it is formed to a  
10           semiconductor fabrication process.

            27. The method of claim 26, wherein the gas is continuously  
            fed as it is produced to a chemical vapor deposition reactor or an  
            oxidation furnace.

15           28. The method of any of claims 24-27, wherein the precursor  
            material is liquid, and wherein the reaction produces a two-phase  
            system including the gas.

20           29. The method of any of claims 24-28, wherein the gas is  
            phosphine.

            30. An apparatus for the fabrication of a semiconductor  
            device, comprising:  
25           a gas generation reactor for generating a gas, the gas  
            generation reactor having a microwave transparent reaction chamber and  
            a source of microwave radiation directed into the reaction chamber;  
            and  
            a chemical vapor deposition reactor or an oxidation furnace  
30           coupled to the gas generation reactor.

            31. The apparatus of claim 30, wherein the gas is phosphine.

            32. A chemical reactor system for generation of high purity  
35           gas for semiconductor fabrication, comprised of:  
            a source of microwave radiation;

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- 21 -

a reaction chamber for receiving a precursor material for generating said gas, said reaction chamber adapted to generate said gas under pressure;

5 a microwave transparent, gas tight barrier through which said source of microwave radiation is directed into said reaction chamber; a microwave reflecting enclosure into which said source of microwave radiation is directed;

10 a manifold for gas delivery adapted to receive the generated gas; and a solvent vapor removal device adapted to remove solvent vapor from the generated gas.

15 33. The system of claim 32, also comprising a supply of precursor material coupled to said reaction chamber.

34. The system of claim 33, also comprising:  
a gas concentration sensor for sensing gas concentration in the generated gas; and

20 a feed-back control system to control gas generation rate in said reaction chamber.

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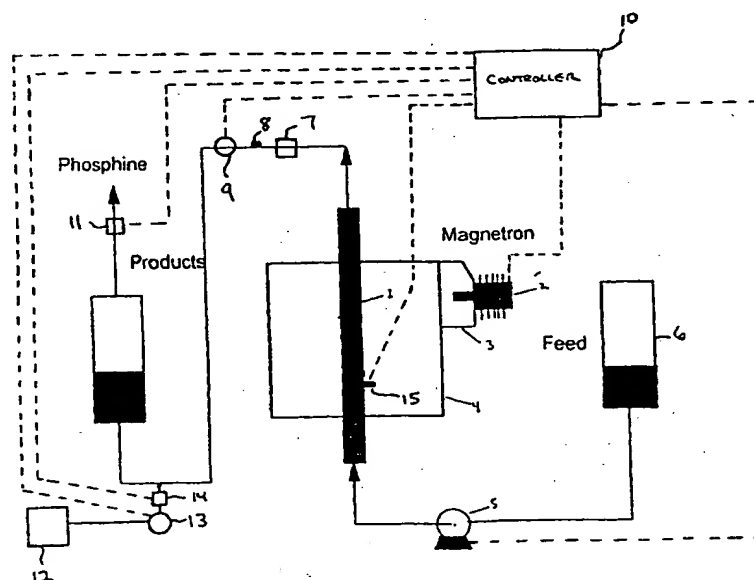
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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US99/15181 <b>(22) International Filing Date:</b> 6 July 1999 (06.07.99) <b>(30) Priority Data:</b> 60/091,737                      6 July 1998 (06.07.98)                      US <b>(71) Applicant (for all designated States except US):</b> ELECTRON TRANSFER TECHNOLOGIES, INC. [US/US]; 155 Campus Drive, P.O. Box 5812, Edison, NJ 08818-5812 (US). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> AYERS, William, M. [US/US]; 372 Carter Road, Princeton, NJ 08540 (US). <b>(74) Agents:</b> GANDY, Kenneth, A. et al.; Woodard, Emhardt, Naughton, Moriarty & McNett, Bank One Center/Tower, Suite 3700, 111 Monument Circle, Indianapolis, IN 46204 (US).		<b>(81) Designated States:</b> CN, JP, US.  <b>Published</b> <i>With international search report.</i>

**(54) Title:** METHOD AND APPARATUS FOR THE PREPARATION OF HIGH PURITY PHOSPHINE OR OTHER GAS

**(57) Abstract**

A chemical apparatus and method for the generation of high purity phosphine gas or another gas used in the production and doping of semiconductors is described. The preferred apparatus includes a means for generating the gas with microwave radiation, a means for controlling the production rate (10), means for purifying the product gas, and a means for controlled blending of the gas with a diluent gas to a desired delivery composition. By these means, gas of sufficient purity, at the proper pressure, and in the required volume, is generated for direct introduction into a process in which semiconductors are manufactured and doped.

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METHOD AND APPARATUS FOR THE PREPARATION  
OF HIGH PURITY PHOSPHINE OR OTHER GAS

5

Background Of The Invention

10 Field of the Invention

This invention relates to the chemical synthesis and production of semiconductor grade gases, such as phosphine, and a reactor for carrying out the synthesis. The synthesis and the reactor are designed to produce high purity gas and deliver it to a semiconductor fabrication process.

Art Related to the Invention

High purity gases, such as phosphine ( $\text{PH}_3$ ), are required for semiconductor fabrication and doping. Phosphine is flammable, extremely toxic, and hazardous. Phosphine has a toxicity exposure limit of 0.3 ppm. Currently, the gas is manufactured in large centralized chemical plants and then delivered to semiconductor fabrication facilities in steel compressed gas cylinders. Compressed gas cylinders store this toxic gas at several thousand pounds per square inch pressure and contain one to forty five pounds of the gas. Hence, transportation, storage, and handling of these compressed gas cylinders present a major toxic gas release hazard to the environment and the workers within the semiconductor facility.

30

On-site synthesis of these gases provides an alternative means to provide such gases to the semiconductor industry in a safe manner. The process and reactor described herein allows the gas to be generated on-site as needed thereby eliminating the transportation, storage, and handling of toxic gas cylinders in a semiconductor fabrication plant.

35

The phosphine gas generator can be used for II-VI crystal growth including organometallic vapor phase epitaxy, and molecular beam epitaxy of InP, GaP, and solid state lasers such as those based on

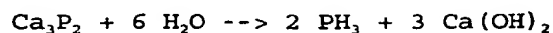
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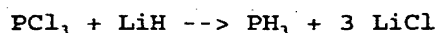
InGaAsP for fiber optic communications. In addition, the phosphine generator can be used as a dopant source for the silicon semiconductor fabrication.

5       The following references disclose processes for producing phosphine gas by chemical methods. Cotton and Wilkinson, Advanced Inorganic Chemistry, 4th Ed., Wiley Interscience (1980); Brauer, Preparative Inorganic Chemistry, Academic Press (1963); and Kirk-Othmer, Encyclopedia of Chemical Technology, Wiley Press.

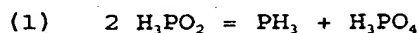
10       Phosphine is traditionally prepared by hydrolysis of white phosphorous or metal phosphides such as:



20       Phosphine can also be prepared by reducing phosphorous chloride with strong reducing agents such as lithium hydride:



25       Other chemical reactions include thermal disproportionations. For example, upon heating above 120° C, hypophosphorous acid ( $H_3PO_2$ ) disproportionates spontaneously to give phosphine and higher oxides of the phosphorous acid. By Thermal Gravimetric Analysis we have  
30       determined that the principal reaction paths are:



35       which consist of the following component reaction paths:

130° C

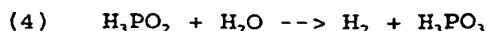


200° C

- 3 -



5 A side reaction which is catalyzed by metals is



10 H.J. Banks and C.J. Waterford, U.S. Pat. No. 5,573,740, disclose a chemical method for generating phosphine based on the reaction of water or water vapor with a metal phosphide. W.Frierel and R. Ehert, U.S. Pat. No. 4,720,380 disclose an aluminum phosphide formulation for generation of phosphine for pesticidal applications. Both methods  
15 produce a dilute, moist phosphine for use as a pesticidal gas. This low concentration, impure gas is unsuitable for semiconductor applications.

C.R. Strauss and A.F. Faux, U.S. Pat. No. 5,387,397, disclose a  
20 method and apparatus for chemical reactions based on feeding reactants through a microwave-heated zone. This method is only appropriate for liquid phase or liquid slurry reactions in which the product is a liquid. No provision is made for phase change and gas product production and expansion within the reaction zone. Furthermore,  
25 Strauss's specification of a small diameter coiled tube in the microwave-heated region precludes refluxing of the chemical reaction in the heated region and hence limits the product yield.

Koch, in U.S. Patent No. 5,529,669 teaches the use of single  
30 mode microwave radiation to raise the temperature of a metal catalyst and thereby increase the reaction rate between ammonia and a hydrocarbon containing gas. Koch feeds two gas phase reactants over a microwave-heated catalyst. The product of the gas phase reaction is another gas, hydrogen cyanide. No phase change or allowances for  
35 phase change is taught in their patent. Furthermore no allowances are made for refluxing of reactants to increase the reaction yield of the products.

- 4 -

T. A. Koch, K.R. Krause, and M. Mehdizadeh (U.S. Pat. Nos. 5,470,541 and 5,529,669) disclose a process for the preparation of hydrogen cyanide. Their method specifies a tubular reactor within a resonant cavity tuned to the TE<sub>011</sub> mode of a microwave source.

5

One major limitation of these inventions is the use of one material (Teflon or glass) as the conduit for exposing the reactants to microwave energy. This limits the type of reactions which can be carried out. Teflon is limited to temperature below 260° C and glass or quartz is attacked and corroded by hot alkali and some acid solutions.

10



- 5 -

Summary Of The Invention

The present invention relates to a chemical process and reactor suitable for producing phosphine or other gases of sufficient purity and at a proper pressure, for direct introduction into a process in which semiconductors are manufactured or doped. These semiconductor manufacturing processes typically include a chemical vapor deposition reactor (hereafter CVD) used for epitaxial growth of phosphorous containing semiconductors or an oxidation furnace used for phosphine doping of semiconductors.

In one embodiment, the invention provides a preferred reactor that includes a source of microwave radiation, a microwave transparent, metal free, gas tight reaction zone or chamber, and a microwave reflecting enclosure. The gas is produced by the interaction of microwave radiation with a precursor material. The precursor preferably is a liquid but in broad aspects may also be a solid, e.g. crystalline  $H_3PO_2$  or crystalline  $H_3PO_3$  for the production of phosphine. Preferably, a liquid precursor such as a solution of an appropriate acid or salt passes through the microwave transparent reaction zone thereby allowing the production of the high purity chemical with minimal by-product reaction contamination. The preferred microwave source can be quickly turned on and off thereby allowing for rapid heating and cooling of the precursor material, and hence the rate of chemical reaction. The microwave radiation predominately heats the precursor with minimal heating of the surrounding containment chamber. In addition, a preferred device provides a phosphine generator having a phosphine source material canister or other container which desirably can be refilled with precursor material and recycled. This can minimize hazardous waste disposal and provide a responsible approach to protecting the environment for the phosphine production and utilization.

One feature of the invention is that it addresses the limitation of use of a single material, such as Teflon or glass, in the microwave heated zone, by the use of composite or multiple (e.g. two)

- 6 -

layer microwave transparent conduits which provide a corrosion barrier and mechanical strength at high temperature and pressures. The preferred microwave transparent material in the reaction zone also is capable of sustaining pressures above one atmosphere and is resistant to corrosion from the chemicals within the reaction zone.

Other advantages of preferred embodiments of the invention include unexpected very high yield production of pure, hydrogen free, phosphine (>99.99%) by the elimination of all non-refractory metals from the reaction zone, and no need for tuned resonant cavity (less expensive to manufacture). We have found that the reactions occur with high selectivity without the need of the specific TE011 microwave radiation mode. In addition, in the reaction zone, liquid or vapor of the reacting material comes into contact with heated non-reacting fluid thereby accelerating heat transfer and the reaction process; very fast heat transfer to the reactant fluid. Still further, the preferred process and reactors provide for reflux of reactants within the microwave heated zone.

In more preferred embodiments, an automated pneumatic manifold for gas delivery can be used to direct the gas to the semiconductor reactor. Preferably located on the manifold are solvent vapor removal cartridges (e.g. containing silica gel) to remove traces of water from the gas, desirably to establish a product (e.g. phosphine) gas that contains no more than 100 parts per million of oxygen or water vapor. Also, a gas concentration sensor, and a feedback control system to control gas pressure and concentration, can be provided. A pressure sensor on the manifold and a microprocessor attached to it can be provided to maintain pressure in the reactor required by the inlet to the CVD to which it is connected, and to provide for suitable flow into it.

A concentration monitor on the manifold, a diluent gas mass flow controller, and a microprocessor attached to both can be used in a preferred apparatus to maintain the concentration of phosphine or other gas leaving the manifold at the desired value.

- 7 -

The preferred system is automatically controlled by a microprocessor, and graphic interface based software. The software control on the system makes it easy to operate, purge and evacuate the system, and to deliver and blend phosphine in the concentration desired. The preferred software also displays the concentration of phosphine in the delivery gas stream in real time, tracks the amount of precursor material left in the supply tank, and displays the amount of phosphine or other gas available for delivery.

10

An electrically grounded temperature probe sealed in Teflon and placed in the two-phase zone can be used to more accurately control the magnetron output without electromagnetic noise from the microwave.

15

Two types of reaction chemistries may be utilized in the generation of phosphine. These are: thermal decomposition of acidic  $\text{H}_3\text{PO}_2$ , and base-catalyzed

- 8 -

hydrolysis of red phosphorous which produces  $H_3PO_2$  as an intermediate compound leading to phosphine generation.

In another embodiment, the present invention provides a method  
5 for generating a high purity gas for semiconductor processing,  
comprising producing the gas by the interaction of microwave radiation  
with a precursor material while said precursor material passes through  
a microwave transparent, metal free, gas impermeable, pressurized  
reaction zone.

10

The present invention also concerns a method for fabricating a  
semiconductor device using a gas, such as phosphine, characterized by  
the use of the gas when produced by the reaction of a precursor  
material under the influence of microwave radiation. In a preferred  
15 mode, such a method comprises producing the gas continuously by a  
continuous introduction and reaction of the precursor material in a  
microwave transparent reaction chamber irradiated with microwave  
radiation. and feeding the produced gas continuously as it is formed  
to a semiconductor fabrication process.

20

In yet another embodiment, the invention provides an apparatus  
for the fabrication of a semiconductor device, comprising a gas  
generation reactor for generating a gas, the gas generation reactor  
having a microwave transparent reaction chamber and a source of  
25 microwave radiation directed into the reaction chamber, and a  
semiconductor fabrication device, such as a chemical vapor deposition  
reactor or an oxidation furnace, coupled to the gas generation  
reactor.

30

Additional embodiments, features and advantages will be apparent  
from the disclosures herein.

Brief Description Of The Drawings

5           Figure 1 provides a diagrammatic view of a preferred reactor of the invention.

          Figure 2 provides a diagrammatic view of another preferred reactor of the invention.

10

          Figure 3 provides a diagrammatic view of another preferred reactor of the invention.

- 10 -

Description Of The Preferred Embodiments

For the purposes of promoting an understanding of the principles of the invention, reference will now be made to  
5 embodiments thereof and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations, further modifications and applications of the principles of the invention as described herein being contemplated as would normally  
10 occur to one skilled in the art to which the invention pertains.

Referring now to FIG. 1, shown is a preferred reactor system of the invention. The reactor includes a reaction chamber tube 1 of a microwave transparent material (e.g. fused silica, silicon dioxide,  
15 boron nitride, graphite or Teflon) that is irradiated with microwave radiation from a radiation source including a magnetron 2 attached to a waveguide 3. This microwave radiation source may, for example, have a frequency of about 0.9 GHz or from about 2.41 to about 10 GHz. The reaction chamber 1 is contained within a microwave reflecting  
20 enclosure 4, for instance constructed of an electrically conductive material desirably having a conductivity of at least about  $10^{-3}$  ohm/cm. The enclosure 4 also preferably has a smallest dimension at least twice the wavelength of the microwave radiation to be employed. At the bottom of the reaction chamber 1 is a high boiling point liquid  
25 (HBPL) such as phosphoric acid or silicon oil which absorbs the microwave radiation.

A pump 5 transports a precursor material, preferably a liquid, from a feed source 6 into the reaction chamber 1 at a fixed or variable, preferably fixed, feed rate. The precursor material is  
30 capable of reacting in the reaction chamber 1 to produce a desired gas. In the production of phosphine, the precursor material may for example be an aqueous solution of  $H_3PO_2$ , an aqueous solution of  $H_3PO_3$ , an aqueous solution of a salt of the formula  $XH_2PO_2$  or  $XH_2PO_3$ , wherein X is an alkali metal such as Li, Na or K, an aqueous solution of a salt  
35 of the formula  $Z_2(H_2PO_2)_2$ , wherein Z is an alkaline earth metal such as Ca, Mg, Sr, or Ba, or an alkaline (e.g. aqueous NaOH, KOH or LiOH)

- 11 -

slurry of red phosphorous. The precursor material flash evaporates and undergoes the disproportionation reaction to phosphine gas when it contacts the heated HBPL. The product phosphine gas and phosphoric acid expand in the tube as a foam with a void fraction of at least about 60%. The reaction chamber is sized to allow for this two-phase expansion.

One key feature of the expansion reaction zone is that it allows refluxing of the mixture. Refluxing within the chamber greatly increases the residence time and hence the yield of the reaction. The two-phase fluid refluxes in the reaction chamber until the reaction yield is at least 70% in preferred embodiments. The phosphine yield is a function of several factors, including the HBPL temperature, feed rate of the precursor solution, reflux, etc.

The preferred phosphine gas generation system can also be operated in a feed-back control mode to provide substantially constant pressure delivery of the gas, analogous to that described in WO 97/20965. In this mode, a pressure sensor 8 and a pressure regulator 9 can be mounted in the gas delivery line. A microprocessor 10 monitors the pressure signal and compares it to a desired set-point pressure. The microprocessor 10 then turns on or off the magnetron 2 to generate phosphine gas and maintain the desired set-point pressure. The microprocessor 10 can also control the sequencing of various valves or other components on the gas delivery manifold. For example, an automated pneumatic manifold for gas delivery can include a solvent vapor removal device or devices (e.g. cartridges containing silica gel) 7 to remove traces of water and/or other undesirable substances from the gas, desirably to establish a product (e.g. phosphine) gas that contains no more than 100 parts per million of oxygen or water vapor. The pressure sensor 8 on the manifold and the associated microprocessor 10 can be used to maintain pressure in the reactor required by the inlet to the CVD to which it is connected, and to provide for suitable flow of precursor material into it. A concentration monitor 11 on the manifold, a source of diluent gas 12, a valve 13, and a diluent gas mass flow controller 14, and the

- 12 -

associated microprocessor can be used in a preferred apparatus to maintain the concentration of phosphine or other gas leaving the manifold at the desired value.

5           The temperature in the HBPL can also be detected by a platinum resistance temperature monitor (RTD) 15 electrically grounded to the magnetron power supply. This provides a steady temperature signal directly from the fluid without interference noise from the microwave radiation. The temperature of the HBPL can be maintained by a feed-  
10 back loop between the RTD and the microprocessor 10 connected to the magnetron power supply.

          The preferred system also includes graphic interface based software. The software control on the system makes it easy to  
15 operate, purge and evacuate the system, and to deliver and blend phosphine or other gases in the concentration desired. The preferred software also displays the concentration of phosphine or other gas in the delivery gas stream in real time, tracks the amount of precursor material left in the supply tank, and displays the amount of phosphine  
20 or other gas available for delivery. The microprocessor controller 10 is preferably remotely linked to a terminal device in a near-by or remote location.

          In another embodiment of the invention, the reactor may include  
25 an inner, corrosion-resistant microwave transparent tube is concentrically surrounded by a second microwave transparent tube capable of withstanding higher pressures. In this manner, higher pressures of phosphine can be produced safely without corroding the outer tube.

30  
          Figure 2 shows another embodiment of the invention. Here the microwave transparent reaction chamber tube is replaced with a microwave transparent flat window mounted on a steel reaction chamber. The reaction chamber 21 is a steel vessel capable of withstanding high  
35 pressures. The top of the chamber has a metal plate in which is mounted the microwave transparent window 22. The window 22 is fixed



- 13 -

to the metal plate with an O-ring or other pressure-tight seal to prevent gas from escaping around the window 22. A wave guide 23 and one or more magnetrons 24 are mounted on the waveguide. Microwave radiation from the magnetron is directed through the microwave transparent window into the fluid 25 held in the reaction chamber.

The window can be made thicker and have a smaller area than the microwave transparent tube shown in Fig. 1. Both of these factors allow the window to withstand higher pressures than the tube configuration. By this means the temperature and pressure limitations of materials currently used in microwave transparent tubes or conduits in the reaction chamber are overcome. This allows higher pressure gas product to be produced with less concern of materials failure and gas leakage from the reactor. The inside of the reaction chamber can also be coated with a corrosion-resistant coating (e.g. tantalum or Tefzel), to eliminate contact of the hot fluid with the chamber walls.

In yet another preferred embodiment of the invention, Fig. 3 illustrates a microwave transparent reflux tube 31 extending partway up the height of a stainless steel vessel 32. Holes in the bottom of the reflux tube allow the HBPL to flow into a concentric outer container 33 thereby controlling the liquid height in the reflux tube. Reaction product phosphoric acid liquid overflows the edge of the outer container and exits the steel vessel through a drain 34. The reactant feed liquid is fed into the center tube 31 where it contacts the hot HBPL and flash evaporates. The reactant liquid and vapor reflux within the center tube until the reaction reaches completion. The product gas exits the steel chamber through a port 35.

It will be understood that the reactor systems illustrated in Figs. 2 and 3 can be equipped with similar manifold and control features to those illustrated in Fig. 1. Thus, the systems of Figs. 2 and 3 can include components corresponding to those numbered 7-15 in Fig. 1.

- 14 -

The following examples illustrate, but do not define or limit, the invention.

EXAMPLE 1

5        One particular configuration for the process for producing phosphine is the thermal decomposition of  $H_3PO_2$ . Phosphine was generated using a vertical tubular reactor made of Teflon-PFA. The reactor had an inside diameter of 0.957 inch, outside diameter of 1.315 inch and total length of 35 inches. The reactor consists of  
10    three zones; an entrance zone (of length 8.5 inches), a microwave irradiated reaction and reflux zone (of length 10 inches) and an overflow zone (of length 16.5 inches). The extended zones of entrance and overflow were used to assist reactant reflux, cooling, and gas-liquid separation of the hot reaction products before they  
15    reach the exit port. The microwave transparent tube was irradiated with approximately 850 watts at 2.45 Ghz.

      The phosphine was generated at  $240^\circ C$  and 25 pounds per square inch outlet pressure. The rate of phosphine gas production proportional to microwave wattage heating the reaction zone. The  
20    liquid feed, 50%  $H_3PO_2$  in water, was pumped into the bottom of the tube at 2.6 and 10.8 milliliters/min. At the liquid feed rate of 2.6ml/min the conversion of  $H_3PO_2$  to  $PH_3$  was 94 % with a phosphine production rate of 260 standard cubic centimeter per minutes (sccm). At a feed rate of 10.8 ml/min the conversion was 73 % with a  
25    phosphine production rate of 850 sccm. In both cases, the purity of the phosphine was greater than 99.99%.

      During microwave heating of the liquid, about 75% of the reactor volume is filled with a two-phase gas liquid foam consisting of phosphorous acids, water vapor, and phosphine. The two-phase  
30    foam refluxes in the reaction zone until it some of it overflows out of the phosphine exit port on the tube. At the end of the production run, the solution remaining in the reactor tube consists over 90%  $H_3PO_4$  in water. This solution is used as the high boiling point liquid heating medium.

- 15 -

By keeping the reaction zone free of metals (including stainless steel and Inconel), extremely high purity, hydrogen free, phosphine was produced. By-product hydrogen can be produced by the reaction:

5



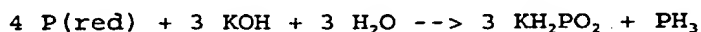
which we have found is catalyzed by transition metals.

#### EXAMPLE 2

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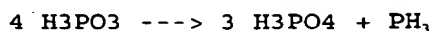
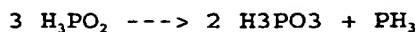
In this example, the raw material for production of high purity phosphine gas consists of a finely divided slurry of red phosphorous powder. Red phosphorous, is a polymeric form of white phosphorous. It is stable in air and water and therefore much safer to use as a precursor material than white phosphorous. We mixed red phosphorous powder (100 mesh size) into a potassium hydroxide solution to produce a slurry. Upon microwave heating of the slurry, we found the following reactions occur:

20



The hypophorous compound can be further decomposed as in Example 1

25



30

By varying the concentration of KOH between 5 and 11 molar and the temperature between 42 and 85° C, we determined that the rate of phosphine generation from this reaction can be described by the equation:

$$\text{rate} = k_o \cdot \exp(-13,780/RT) \cdot [\text{OH-}]^3$$

35

where  $k_o = 0.55$  and rate is expressed as moles of  $\text{PH}_3$  produced per gram of red phosphorous per second of reaction time. By this means we have found that one standard liter per minute of  $\text{PH}_3$  can be produced by the thermal reaction of 34.4 grams of  $\text{P}(\text{red})$  per minute

- 16 -

at 85° C. Faster production rates of phosphine can be produced at higher temperatures up to the material limits of the reaction zone material.

5

EXAMPLE 3

In a modification of the process, some applications for semiconductor growth may require a different phosphine concentration than produced by the generator. With conventional gas cylinders, different gas concentrations would have to be pre-mixed to the desired concentration before filling the gas cylinder. In a modification of the phosphine generator, a feedback loop is used to control the mixing of the two gases and thereby maintain the desired gas concentration. This makes phosphine generator more versatile in that it can provide a wide range of gas concentrations.

15 The operator of the phosphine generator desires to provide 50% phosphine in hydrogen to the CVD deposition reactor. The operator selects this desired concentration from the software program. The microprocessor then determines the concentration of phosphine flowing through a concentration sensor. The computer program compares this concentration to the set point or desired concentration. A mass flow controller (MFC) then allows a diluting gas, hydrogen, to flow into a mixing tee where it is completely mixed with the phosphine.

25 The mixed gas then enters the concentration monitor with the mixed final concentration is determined. The MFC is then directed by the PC program to increase or decrease the diluent flow to maintain the set point concentration value. By this means, the operator can set and control any concentration between 0% and the maximum phosphine concentration produced by the generator.

30

- 17 -

I claim:

1. A method of generating high purity phosphine gas, comprising producing phosphine gas by the interaction of microwave radiation with a precursor material while said precursor material passes through a microwave transparent, metal free, gas impermeable, pressurized reaction zone.
2. The method of Claim 1 wherein the precursor material is  $H_3PO_2$  in an aqueous solution.
3. The method of Claim 1 wherein the precursor material is  $H_3PO_3$  in an aqueous solution.
4. The method of Claim 1 wherein the precursor material is crystalline  $H_3PO_2$  or crystalline  $H_3PO_3$ .
5. The method of Claim 1 wherein the precursor material is a salt of the formula  $XH_2PO_2$  in an aqueous solution where X is selected from the alkali metals group consisting of Li, Na, and K.
6. The method of Claim 1 wherein the precursor material is a salt of the formula  $X_2(H_2PO_2)_2$  in an aqueous solution where X is selected from the alkaline metals group consisting of Ca, Mg, Sr, and Ba.
7. The method of Claim 1 wherein the precursor material is a salt of the formula  $XH_2PO_3$  in an aqueous solution where X is selected from the alkali metals group consisting of Li, Na, and K.
8. The method of Claim 1 wherein the precursor material is a slurry of red phosphorus in an alkaline solution.
9. The method of Claim 8 wherein the alkaline solution is selected from the group consisting of NaOH, KOH, and LiOH dissolved in water or combinations thereof.

- 18 -

10. The method of Claim 1 wherein the high purity gas contains no more than 100 parts per million of oxygen or water vapor.

5 11. A chemical reactor system for generation of high purity gas, comprised of a source of microwave radiation, a microwave transparent, gas tight barrier, a microwave reflecting enclosure into which said source of microwave radiation is directed, a manifold for gas delivery adapted to receive generated gas from said enclosure, a  
10 solvent vapor removal device adapted to remove solvent vapor from the generated gas, a gas concentration sensor for sensing gas concentration in the generated gas, and a feed-back control system to control gas generation rate in said enclosure.

15 12. The system of Claim 11, wherein the microwave radiation source has a frequency of 0.9 GHz, or 2.41 to 10 GHz.

13. The system of Claim 11, wherein the microwave transparent barrier is constructed from materials chosen from the group Teflon,  
20 fused silica, silicon dioxide, boron nitride, or graphite.

14. The system of Claim 11, wherein the microwave reflecting enclosure is constructed from an electrically conductive material with a conductivity of a least  $10^{-3}$  ohm/cm.

25 15. The system of Claim 11, wherein the microwave reflecting enclosure has a smallest dimension of at least twice the wavelength of the microwave radiation.

30 16. The system of Claim 11 wherein the precursor material is selected from the group consisting of hypophosphorous acid, hypophoric acid, and an alkaline slurry of red phosphorous.

35 17. The system of Claim 11 wherein the vapor removal device contains silica gel.

- 19 -

18. The system of Claim 11, wherein the feedback control system includes a microprocessor controlled temperature feedback loop to a raw material feed pump, and microwave radiation source power supply.

5

19. The system of Claim 11 wherein the feedback control system modulates the electrical power to the microwave radiation source to maintain a constant gas delivery pressure.

10

20. The system of Claim 11 wherein the feedback control system modulates the electrical power to the microwave radiation source to provide a variable gas flow rate.

15

21. The system of Claim 11 wherein the feedback control system modulates the microwave radiation frequency to control the reaction product selectivity.

20

22. A concentration control system for phosphine product gas, comprising:

a concentration monitor for measuring the ratio of phosphine to diluting gas in a product gas stream;

a microprocessor based comparitor to determine the present concentration versus a desired concentration of phosphine gas in the product gas stream; and

25

a gas flow controller to control the introduction of a diluting gas into the product gas stream in response to a signal generated based on said determination.

30

23. The system of claim 22, wherein the phosphine gas is generated by reaction of a precursor material under the influence of microwave radiation.

35

24. A method for generating a high purity gas for semiconductor processing, comprising producing the gas by the interaction of microwave radiation with a precursor material while

- 20 -

said precursor material passes through a microwave transparent, metal free, gas impermeable, pressurized reaction zone.

25. A method for fabricating a semiconductor device using a gas, characterized by the use of the gas when produced by the reaction of a precursor material under the influence of microwave radiation.

26. The method of claim 25, which comprises:  
producing the gas continuously by a continuous introduction and reaction of the precursor material in a microwave transparent reaction chamber irradiated with microwave radiation; and  
feeding the produced gas continuously as it is formed to a semiconductor fabrication process.

27. The method of claim 26, wherein the gas is continuously fed as it is produced to a chemical vapor deposition reactor or an oxidation furnace.

28. The method of any of claims 24-27, wherein the precursor material is liquid, and wherein the reaction produces a two-phase system including the gas.

29. The method of any of claims 24-28, wherein the gas is phosphine.

30. An apparatus for the fabrication of a semiconductor device, comprising:

a gas generation reactor for generating a gas, the gas generation reactor having a microwave transparent reaction chamber and a source of microwave radiation directed into the reaction chamber; and

a chemical vapor deposition reactor or an oxidation furnace coupled to the gas generation reactor.

31. The apparatus of claim 30, wherein the gas is phosphine.





Fig. 2

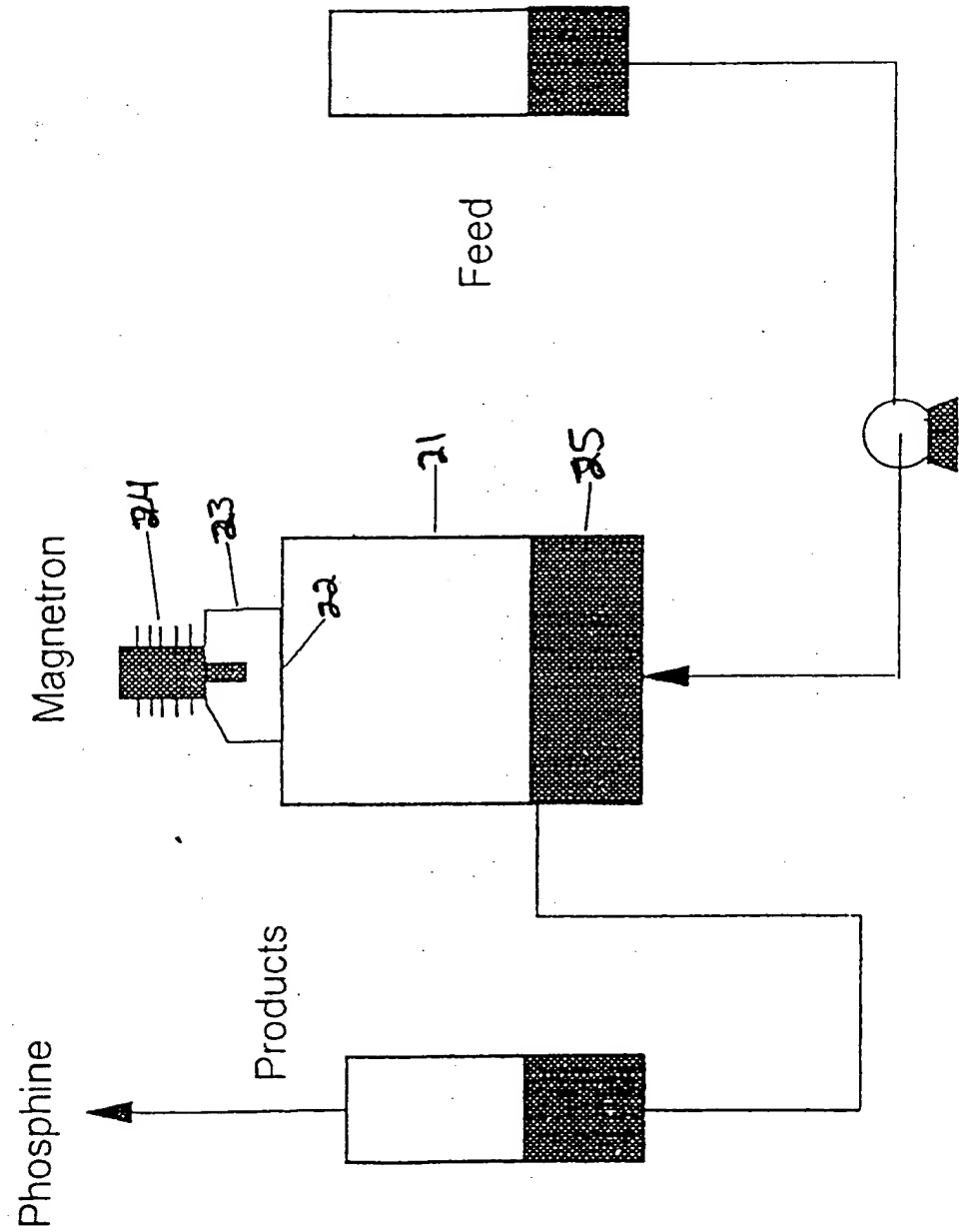
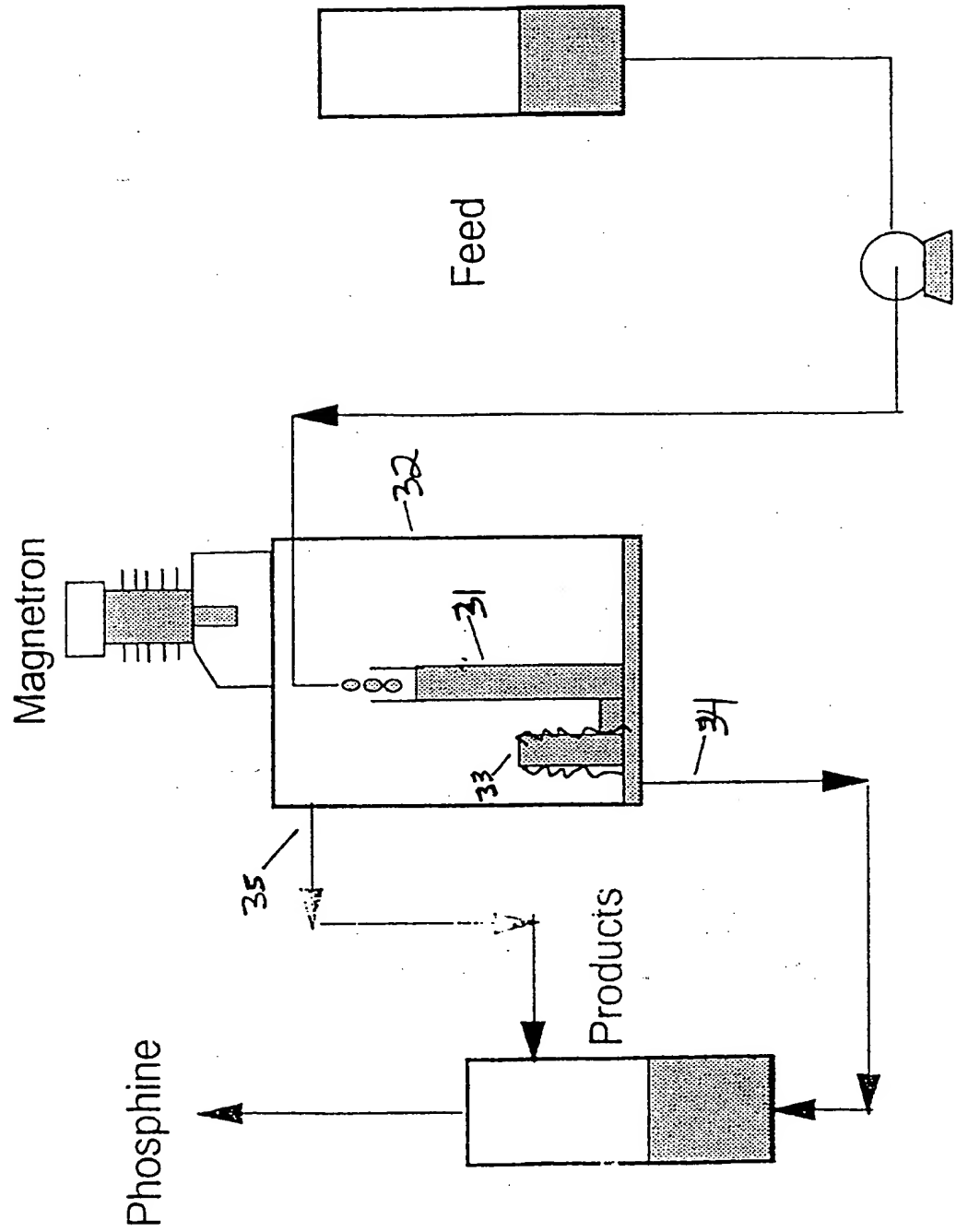


Fig. 3



526 Rec'd PCT/PTO 28 DEC 2000

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/15181

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C01B 53/00; H05B 6/50; A61L 2/00; A47J 37/08; C23C 16/00

US CL : 204/157.43; 219/707; 422/21; 96/397; 438/800, 935; 118/715

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 204/157.43; 219/707; 422/21; 96/397; 438/ 800, 935; 118/715

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST

search terms: phosphine, microwave

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,E ----- Y,E	US 5,951,831 A (GODBER ET AL.) 14 September 1999, col. 8, Example XVII.	1,3 ----- 10, 24-25
Y	US 5,569,726 A (OISHI ET AL.) 29 October 1996, col. 23, line 47 to col. 24, line 10.	2,4-9
Y	EP 454,122 A2 (KAWASAKI JUKOGYO KABUSHIKI KAISHA) 30 October 1991, page 8, line 17 to page 9, line 31 and Figs. 6-8.	11-21
X,E	US 5,925,232 A (AYERS) 20 July 1999, col. 4, lines 32-50 and Fig. 1.	22-23
Y	US 5,158,656 A (AYERS) 27 October 1992, col. 2, lines 25-40; col. 2, line 50 to col. 3, line 12; and Fig. 1.	26-31



Further documents are listed in the continuation of Box C.



See patent family annex.

* *A* *B* *L* *O* *P*	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance earlier document published on or after the international filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	*T* *X* *Y* *A*	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family
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Date of the actual completion of the international search

20 SEPTEMBER 1999

Date of mailing of the international search report

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Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer:

EDNA WONG

Telephone No. (703) 305-0661

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/15181

### BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-10 and 24-31, drawn to a method of generating high purity phosphine gas, a method for generating a high purity gas, a method for fabricating a semiconductor device using gas and an apparatus for the fabrication of a semiconductor device.

Group II, claim(s) 11-21, drawn to a chemical reactor system.

Group III, claim(s) 22-23, drawn to a concentration control system.

The inventions listed as Groups I-III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Group I does not require the use of the system components claimed in Groups II and III.

Group II is a microwave system.

Group III is not a microwave system.



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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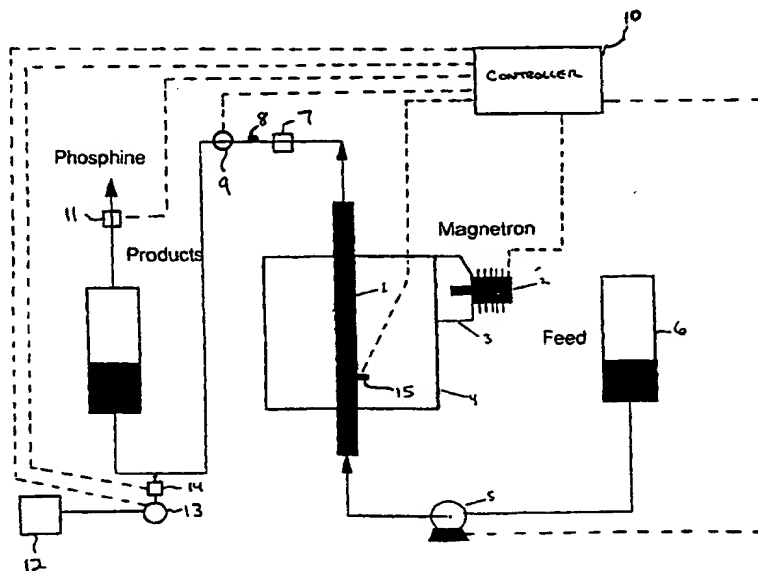
US

(71) Applicant (for all designated States except US): ELECTRON  
TRANSFER TECHNOLOGIES, INC. [US/US]; 155 Cam-  
pus Drive, P.O. Box 5812, Edison, NJ 08818-5812 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): AYERS, William, M.  
[US/US]; 372 Carter Road, Princeton, NJ 08540 (US).(74) Agents: GANDY, Kenneth, A. et al.; Woodard, Emhardt,  
Naughton, Moriarty & McNett, Bank One Center/Tower,  
Suite 3700, 111 Monument Circle, Indianapolis, IN 46204  
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(54) Title: METHOD AND APPARATUS FOR THE PREPARATION OF HIGH PURITY PHOSPHINE OR OTHER GAS



## (57) Abstract

A chemical apparatus and method for the generation of high purity phosphine gas or another gas used in the production and doping of semiconductors is described. The preferred apparatus includes a means for generating the gas with microwave radiation, a means for controlling the production rate (10), means for purifying the product gas, and a means for controlled blending of the gas with a diluent gas to a desired delivery composition. By these means, gas of sufficient purity, at the proper pressure, and in the required volume, is generated for direct introduction into a process in which semiconductors are manufactured and doped.

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(74) Agents: GANDY, Kenneth, A. et al.; Woodard, Emhardt,  
Naughton, Moriarty & McNett, Bank One Center/Tower,  
Suite 3700, 111 Monument Circle, Indianapolis, IN 46204  
(US).

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(71) Applicant (*for all designated States except US*): ELEC-  
TRON TRANSFER TECHNOLOGIES, INC. [US/US];  
155 Campus Drive, P.O. Box 5812, Edison, NJ 08818-5812  
(US).

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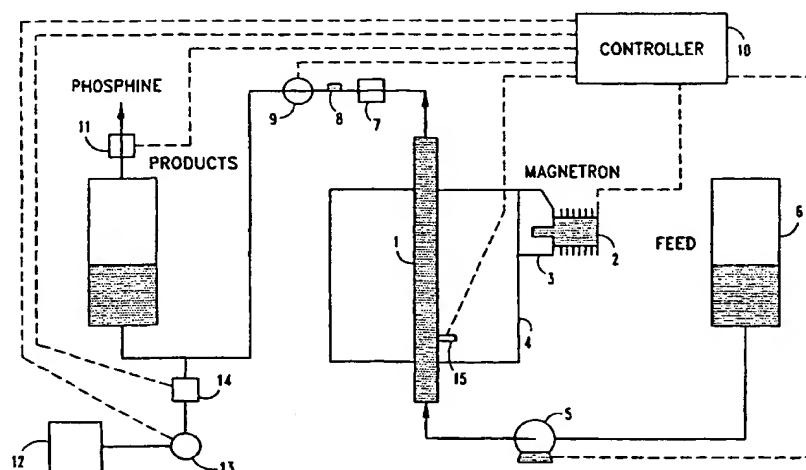
(72) Inventor; and

(75) Inventor/Applicant (*for US only*): AYERS, William, M.  
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(54) Title: METHOD AND APPARATUS FOR THE PREPARATION OF HIGH PURITY PHOSPHINE OR OTHER GAS



(57) Abstract: A chemical apparatus and method for the generation of high purity phosphine gas or another gas used in the production and doping of semiconductors is described. The preferred apparatus includes a means for generating the gas with microwave radiation, a means for controlling the production rate (10), means for purifying the product gas, and a means for controlled blending of the gas with a diluent gas to a desired delivery composition. By these means, gas of sufficient purity, at the proper pressure, and in the required volume, is generated for direct introduction into a process in which semiconductors are manufactured and doped.

WO 00/01615 A1



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METHOD AND APPARATUS FOR THE PREPARATION  
OF HIGH PURITY PHOSPHINE OR OTHER GAS

5

Background Of The Invention

10 Field of the Invention

This invention relates to the chemical synthesis and production of semiconductor grade gases, such as phosphine, and a reactor for carrying out the synthesis. The synthesis and the reactor are designed to produce high purity gas and deliver it to a semiconductor fabrication process.

15

Art Related to the Invention

High purity gases, such as phosphine ( $\text{PH}_3$ ), are required for semiconductor fabrication and doping. Phosphine is flammable, extremely toxic, and hazardous. Phosphine has a toxicity exposure limit of 0.3 ppm. Currently, the gas is manufactured in large centralized chemical plants and then delivered to semiconductor fabrication facilities in steel compressed gas cylinders. Compressed gas cylinders store this toxic gas at several thousand pounds per square inch pressure and contain one to forty five pounds of the gas. Hence, transportation, storage, and handling of these compressed gas cylinders present a major toxic gas release hazard to the environment and the workers within the semiconductor facility.

20  
25  
30

On-site synthesis of these gases provides an alternative means to provide such gases to the semiconductor industry in a safe manner. The process and reactor described herein allows the gas to be generated on-site as needed thereby eliminating the transportation, storage, and handling of toxic gas cylinders in a semiconductor fabrication plant.

35

The phosphine gas generator can be used for II-VI crystal growth including organometallic vapor phase epitaxy, and molecular beam epitaxy of InP, GaP, and solid state lasers such as those based on

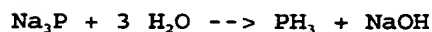
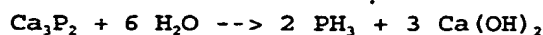
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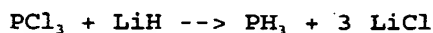
InGaAsP for fiber optic communications. In addition, the phosphine generator can be used as a dopant source for the silicon semiconductor fabrication.

5 The following references disclose processes for producing phosphine gas by chemical methods. Cotton and Wilkinson, Advanced Inorganic Chemistry, 4th Ed., Wiley Interscience (1980); Brauer, Preparative Inorganic Chemistry, Academic Press (1963); and Kirk-Othmer, Encyclopedia of Chemical Technology, Wiley Press.

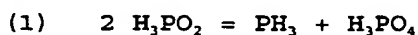
10 Phosphine is traditionally prepared by hydrolysis of white phosphorous or metal phosphides such as:



20 Phosphine can also be prepared by reducing phosphorous chloride with strong reducing agents such as lithium hydride:



25 Other chemical reactions include thermal disproportionations. For example, upon heating above 120° C, hypophosphorous acid (H<sub>3</sub>PO<sub>2</sub>) disproportionates spontaneously to give phosphine and higher oxides of the phosphorous acid. By Thermal Gravimetric Analysis we have  
30 determined that the principal reaction paths are:



35 which consist of the following component reaction paths:

130° C

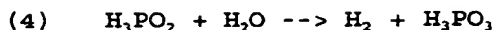


200° C

- 3 -



5 A side reaction which is catalyzed by metals is



10 H.J. Banks and C.J. Waterford, U.S. Pat. No. 5,573,740, disclose a chemical method for generating phosphine based on the reaction of water or water vapor with a metal phosphide. W.Frierel and R. Ehert, U.S. Pat. No. 4,720,380 disclose an aluminum phosphide formulation for generation of phosphine for pesticidal applications. Both methods  
15 produce a dilute, moist phosphine for use as a pesticidal gas. This low concentration, impure gas is unsuitable for semiconductor applications.

C.R. Strauss and A.F. Faux, U.S. Pat. No. 5,387,397, disclose a  
20 method and apparatus for chemical reactions based on feeding reactants through a microwave-heated zone. This method is only appropriate for liquid phase or liquid slurry reactions in which the product is a liquid. No provision is made for phase change and gas product production and expansion within the reaction zone. Furthermore,  
25 Strauss's specification of a small diameter coiled tube in the microwave-heated region precludes refluxing of the chemical reaction in the heated region and hence limits the product yield.

Koch, in U.S. Patent No. 5,529,669 teaches the use of single  
30 mode microwave radiation to raise the temperature of a metal catalyst and thereby increase the reaction rate between ammonia and a hydrocarbon containing gas. Koch feeds two gas phase reactants over a microwave-heated catalyst. The product of the gas phase reaction is another gas, hydrogen cyanide. No phase change or allowances for  
35 phase change is taught in their patent. Furthermore no allowances are made for refluxing of reactants to increase the reaction yield of the products.

- 4 -

T. A. Koch, K.R. Krause, and M. Mehdizadeh (U.S. Pat. Nos. 5,470,541 and 5,529,669) disclose a process for the preparation of hydrogen cyanide. Their method specifies a tubular reactor within a resonant cavity tuned to the TE011 mode of a microwave source.

5

One major limitation of these inventions is the use of one material (Teflon or glass) as the conduit for exposing the reactants to microwave energy. This limits the type of reactions which can be carried out. Teflon is limited to temperature below 260° C and glass or quartz is attacked and corroded by hot alkali and some acid solutions.

10



- 5 -

Summary Of The Invention

The present invention relates to a chemical process and reactor suitable for producing phosphine or other gases of sufficient purity and at a proper pressure, for direct introduction into a process in which semiconductors are manufactured or doped. These semiconductor manufacturing processes typically include a chemical vapor deposition reactor (hereafter CVD) used for epitaxial growth of phosphorous containing semiconductors or an oxidation furnace used for phosphine doping of semiconductors.

In one embodiment, the invention provides a preferred reactor that includes a source of microwave radiation, a microwave transparent, metal free, gas tight reaction zone or chamber, and a microwave reflecting enclosure. The gas is produced by the interaction of microwave radiation with a precursor material. The precursor preferably is a liquid but in broad aspects may also be a solid, e.g. crystalline  $H_3PO_2$  or crystalline  $H_3PO_3$  for the production of phosphine. Preferably, a liquid precursor such as a solution of an appropriate acid or salt passes through the microwave transparent reaction zone thereby allowing the production of the high purity chemical with minimal by-product reaction contamination. The preferred microwave source can be quickly turned on and off thereby allowing for rapid heating and cooling of the precursor material, and hence the rate of chemical reaction. The microwave radiation predominately heats the precursor with minimal heating of the surrounding containment chamber. In addition, a preferred device provides a phosphine generator having a phosphine source material canister or other container which desirably can be refilled with precursor material and recycled. This can minimize hazardous waste disposal and provide a responsible approach to protecting the environment for the phosphine production and utilization.

One feature of the invention is that it addresses the limitation of use of a single material, such as Teflon or glass, in the microwave heated zone, by the use of composite or multiple (e.g. two)

- 6 -

layer microwave transparent conduits which provide a corrosion barrier and mechanical strength at high temperature and pressures. The preferred microwave transparent material in the reaction zone also is capable of sustaining pressures above one atmosphere and is resistant to corrosion from the chemicals within the reaction zone.

Other advantages of preferred embodiments of the invention include unexpected very high yield production of pure, hydrogen free, phosphine (>99.99%) by the elimination of all non-refractory metals from the reaction zone, and no need for tuned resonant cavity (less expensive to manufacture). We have found that the reactions occur with high selectivity without the need of the specific TE011 microwave radiation mode. In addition, in the reaction zone, liquid or vapor of the reacting material comes into contact with heated non-reacting fluid thereby accelerating heat transfer and the reaction process; very fast heat transfer to the reactant fluid. Still further, the preferred process and reactors provide for reflux of reactants within the microwave heated zone.

In more preferred embodiments, an automated pneumatic manifold for gas delivery can be used to direct the gas to the semiconductor reactor. Preferably located on the manifold are solvent vapor removal cartridges (e.g. containing silica gel) to remove traces of water from the gas, desirably to establish a product (e.g. phosphine) gas that contains no more than 100 parts per million of oxygen or water vapor. Also, a gas concentration sensor, and a feedback control system to control gas pressure and concentration, can be provided. A pressure sensor on the manifold and a microprocessor attached to it can be provided to maintain pressure in the reactor required by the inlet to the CVD to which it is connected, and to provide for suitable flow into it.

A concentration monitor on the manifold, a diluent gas mass flow controller, and a microprocessor attached to both can be used in a preferred apparatus to maintain the concentration of phosphine or other gas leaving the manifold at the desired value.

- 7 -

The preferred system is automatically controlled by a microprocessor, and graphic interface based software. The software control on the system makes it easy to operate, purge and evacuate the system, and to deliver and blend phosphine in the concentration  
5 desired. The preferred software also displays the concentration of phosphine in the delivery gas stream in real time, tracks the amount of precursor material left in the supply tank, and displays the amount of phosphine or other gas available for delivery.

10

An electrically grounded temperature probe sealed in Teflon and placed in the two-phase zone can be used to more accurately control the magnetron output without electromagnetic noise from the microwave.

15

Two types of reaction chemistries may be utilized in the generation of phosphine. These are: thermal decomposition of acidic  $H_3PO_3$ , and base-catalyzed

- 8 -

hydrolysis of red phosphorous which produces  $H_3PO_2$  as an intermediate compound leading to phosphine generation.

5 In another embodiment, the present invention provides a method for generating a high purity gas for semiconductor processing, comprising producing the gas by the interaction of microwave radiation with a precursor material while said precursor material passes through a microwave transparent, metal free, gas impermeable, pressurized reaction zone.

10

The present invention also concerns a method for fabricating a semiconductor device using a gas, such as phosphine, characterized by the use of the gas when produced by the reaction of a precursor material under the influence of microwave radiation. In a preferred mode, such a method comprises producing the gas continuously by a continuous introduction and reaction of the precursor material in a microwave transparent reaction chamber irradiated with microwave radiation. and feeding the produced gas continuously as it is formed to a semiconductor fabrication process.

20

In yet another embodiment, the invention provides an apparatus for the fabrication of a semiconductor device, comprising a gas generation reactor for generating a gas, the gas generation reactor having a microwave transparent reaction chamber and a source of microwave radiation directed into the reaction chamber, and a semiconductor fabrication device, such as a chemical vapor deposition reactor or an oxidation furnace, coupled to the gas generation reactor.

25

30 Additional embodiments, features and advantages will be apparent from the disclosures herein.

Brief Description Of The Drawings

5           Figure 1 provides a diagrammatic view of a preferred reactor of the invention.

          Figure 2 provides a diagrammatic view of another preferred reactor of the invention.

10

          Figure 3 provides a diagrammatic view of another preferred reactor of the invention.

- 10 -

Description Of The Preferred Embodiments

For the purposes of promoting an understanding of the principles of the invention, reference will now be made to  
5 embodiments thereof and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations, further modifications and applications of the principles of the invention as described herein being contemplated as would normally  
10 occur to one skilled in the art to which the invention pertains.

Referring now to FIG. 1, shown is a preferred reactor system of the invention. The reactor includes a reaction chamber tube 1 of a microwave transparent material (e.g. fused silica, silicon dioxide,  
15 boron nitride, graphite or Teflon) that is irradiated with microwave radiation from a radiation source including a magnetron 2 attached to a waveguide 3. This microwave radiation source may, for example, have a frequency of about 0.9 GHz or from about 2.41 to about 10 GHz. The reaction chamber 1 is contained within a microwave reflecting  
20 enclosure 4, for instance constructed of an electrically conductive material desirably having a conductivity of at least about  $10^{-3}$  ohm/cm. The enclosure 4 also preferably has a smallest dimension at least twice the wavelength of the microwave radiation to be employed. At the bottom of the reaction chamber 1 is a high boiling point liquid  
25 (HBPL) such as phosphoric acid or silicon oil which absorbs the microwave radiation.

A pump 5 transports a precursor material, preferably a liquid, from a feed source 6 into the reaction chamber 1 at a fixed or variable, preferably fixed, feed rate. The precursor material is  
30 capable of reacting in the reaction chamber 1 to produce a desired gas. In the production of phosphine, the precursor material may for example be an aqueous solution of  $H_3PO_2$ , an aqueous solution of  $H_3PO_3$ , an aqueous solution of a salt of the formula  $XH_2PO_2$  or  $XH_2PO_3$ , wherein X is an alkali metal such as Li, Na or K, an aqueous solution of a salt  
35 of the formula  $Z_2(H_2PO_2)_2$ , wherein Z is an alkaline earth metal such as Ca, Mg, Sr, or Ba, or an alkaline (e.g. aqueous NaOH, KOH or LiOH)

- 11 -

slurry of red phosphorous. The precursor material flash evaporates and undergoes the disproportionation reaction to phosphine gas when it contacts the heated HBPL. The product phosphine gas and phosphoric acid expand in the tube as a foam with a void fraction of at least  
5 about 60%. The reaction chamber is sized to allow for this two-phase expansion.

One key feature of the expansion reaction zone is that it allows refluxing of the mixture. Refluxing within the chamber greatly  
10 increases the residence time and hence the yield of the reaction. The two-phase fluid refluxes in the reaction chamber until the reaction yield is at least 70% in preferred embodiments. The phosphine yield is a function of several factors, including the HBPL temperature, feed rate of the precursor solution, reflux, etc.

15 The preferred phosphine gas generation system can also be operated in a feed-back control mode to provide substantially constant pressure delivery of the gas, analogous to that described in WO 97/20965. In this mode, a pressure sensor 8 and a pressure regulator  
20 9 can be mounted in the gas delivery line. A microprocessor 10 monitors the pressure signal and compares it to a desired set-point pressure. The microprocessor 10 then turns on or off the magnetron 2 to generate phosphine gas and maintain the desired set-point pressure. The microprocessor 10 can also control the sequencing of various  
25 valves or other components on the gas delivery manifold. For example, an automated pneumatic manifold for gas delivery can include a solvent vapor removal device or devices (e.g. cartridges containing silica gel) 7 to remove traces of water and/or other undesirable substances from the gas, desirably to establish a product (e.g. phosphine) gas  
30 that contains no more than 100 parts per million of oxygen or water vapor. The pressure sensor 8 on the manifold and the associated microprocessor 10 can be used to maintain pressure in the reactor required by the inlet to the CVD to which it is connected, and to provide for suitable flow of precursor material into it. A  
35 concentration monitor 11 on the manifold, a source of diluent gas 12, a valve 13, and a diluent gas mass flow controller 14, and the

- 12 -

associated microprocessor can be used in a preferred apparatus to maintain the concentration of phosphine or other gas leaving the manifold at the desired value.

5           The temperature in the HBPL can also be detected by a platinum resistance temperature monitor (RTD) 15 electrically grounded to the magnetron power supply. This provides a steady temperature signal directly from the fluid without interference noise from the microwave radiation. The temperature of the HBPL can be maintained by a feed-  
10 back loop between the RTD and the microprocessor 10 connected to the magnetron power supply.

          The preferred system also includes graphic interface based software. The software control on the system makes it easy to  
15 operate, purge and evacuate the system, and to deliver and blend phosphine or other gases in the concentration desired. The preferred software also displays the concentration of phosphine or other gas in the delivery gas stream in real time, tracks the amount of precursor material left in the supply tank, and displays the amount of phosphine  
20 or other gas available for delivery. The microprocessor controller 10 is preferably remotely linked to a terminal device in a near-by or remote location.

          In another embodiment of the invention, the reactor may include  
25 an inner, corrosion-resistant microwave transparent tube is concentrically surrounded by a second microwave transparent tube capable of withstanding higher pressures. In this manner, higher pressures of phosphine can be produced safely without corroding the outer tube.

30

          Figure 2 shows another embodiment of the invention. Here the microwave transparent reaction chamber tube is replaced with a microwave transparent flat window mounted on a steel reaction chamber. The reaction chamber 21 is a steel vessel capable of withstanding high  
35 pressures. The top of the chamber has a metal plate in which is mounted the microwave transparent window 22. The window 22 is fixed



- 13 -

to the metal plate with an O-ring or other pressure-tight seal to prevent gas from escaping around the window 22. A wave guide 23 and one or more magnetrons 24 are mounted on the waveguide. Microwave radiation from the magnetron is directed through the microwave transparent window into the fluid 25 held in the reaction chamber.

The window can be made thicker and have a smaller area than the microwave transparent tube shown in Fig. 1. Both of these factors allow the window to withstand higher pressures than the tube configuration. By this means the temperature and pressure limitations of materials currently used in microwave transparent tubes or conduits in the reaction chamber are overcome. This allows higher pressure gas product to be produced with less concern of materials failure and gas leakage from the reactor. The inside of the reaction chamber can also be coated with a corrosion-resistant coating (e.g. tantalum or Tefzel), to eliminate contact of the hot fluid with the chamber walls.

In yet another preferred embodiment of the invention, Fig. 3 illustrates a microwave transparent reflux tube 31 extending partway up the height of a stainless steel vessel 32. Holes in the bottom of the reflux tube allow the HBPL to flow into a concentric outer container 33 thereby controlling the liquid height in the reflux tube. Reaction product phosphoric acid liquid overflows the edge of the outer container and exits the steel vessel through a drain 34. The reactant feed liquid is fed into the center tube 31 where it contacts the hot HBPL and flash evaporates. The reactant liquid and vapor reflux within the center tube until the reaction reaches completion. The product gas exits the steel chamber through a port 35.

It will be understood that the reactor systems illustrated in Figs. 2 and 3 can be equipped with similar manifold and control features to those illustrated in Fig. 1. Thus, the systems of Figs. 2 and 3 can include components corresponding to those numbered 7-15 in Fig. 1.

35

- 14 -

The following examples illustrate, but do not define or limit, the invention.

EXAMPLE 1

5           One particular configuration for the process for producing phosphine is the thermal decomposition of  $\text{H}_3\text{PO}_2$ . Phosphine was generated using a vertical tubular reactor made of Teflon-PFA. The reactor had an inside diameter of 0.957 inch, outside diameter of 1.315 inch and total length of 35 inches. The reactor consists of  
10 three zones; an entrance zone (of length 8.5 inches), a microwave irradiated reaction and reflux zone (of length 10 inches) and an overflow zone (of length 16.5 inches). The extended zones of entrance and overflow were used to assist reactant reflux, cooling, and gas-liquid separation of the hot reaction products before they  
15 reach the exit port. The microwave transparent tube was irradiated with approximately 850 watts at 2.45 Ghz.

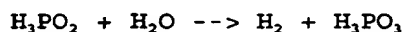
The phosphine was generated at  $240^\circ\text{C}$  and 25 pounds per square inch outlet pressure. The rate of phosphine gas production proportional to microwave wattage heating the reaction zone. The  
20 liquid feed, 50%  $\text{H}_3\text{PO}_2$  in water, was pumped into the bottom of the tube at 2.6 and 10.8 milliliters/min. At the liquid feed rate of 2.6ml/min the conversion of  $\text{H}_3\text{PO}_2$  to  $\text{PH}_3$  was 94 % with a phosphine production rate of 260 standard cubic centimeter per minutes (sccm). At a feed rate of 10.8 ml/min the conversion was 73 % with a  
25 phosphine production rate of 850 sccm. In both cases, the purity of the phosphine was greater than 99.99%.

During microwave heating of the liquid, about 75% of the reactor volume is filled with a two-phase gas liquid foam consisting of phosphorous acids, water vapor, and phosphine. The two-phase  
30 foam refluxes in the reaction zone until it some of it overflows out of the phosphine exit port on the tube. At the end of the production run, the solution remaining in the reactor tube consists over 90%  $\text{H}_3\text{PO}_4$  in water. This solution is used as the high boiling point liquid heating medium.

- 15 -

By keeping the reaction zone free of metals (including stainless steel and Inconel), extremely high purity, hydrogen free, phosphine was produced. By-product hydrogen can be produced by the reaction:

5

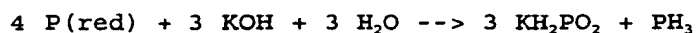


which we have found is catalyzed by transition metals.

#### EXAMPLE 2

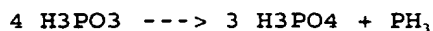
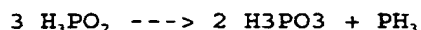
10 In this example, the raw material for production of high purity phosphine gas consists of a finely divided slurry of red phosphorous powder. Red phosphorous, is a polymeric form of white phosphorous. It is stable in air and water and therefore much safer to use as a precursor material than white phosphorous. We mixed red  
15 phosphorous powder (100 mesh size) into a potassium hydroxide solution to produce a slurry. Upon microwave heating of the slurry, we found the following reactions occur:

20



The hypophorous compound can be further decomposed as in Example 1

25



30

By varying the concentration of KOH between 5 and 11 molar and the temperature between 42 and 85° C, we determined that the rate of phosphine generation from this reaction can be described by the equation:

$$\text{rate} = k_o \cdot \exp(-13,780/RT) \cdot [\text{OH}]^3$$

35

where  $k_o = 0.55$  and rate is expressed as moles of  $\text{PH}_3$  produced per gram of red phosphorous per second of reaction time. By this means we have found that one standard liter per minute of  $\text{PH}_3$  can be produced by the thermal reaction of 34.4 grams of P(red) per minute

- 16 -

at 85° C. Faster production rates of phosphine can be produced at higher temperatures up to the material limits of the reaction zone material.

5

EXAMPLE 3

In a modification of the process, some applications for semiconductor growth may require a different phosphine concentration than produced by the generator. With conventional gas cylinders, different gas concentrations would have to be pre-mixed to the desired concentration before filling the gas cylinder. In a modification of the phosphine generator, a feedback loop is used to control the mixing of the two gases and thereby maintain the desired gas concentration. This makes phosphine generator more versatile in that it can provide a wide range of gas concentrations.

15

The operator of the phosphine generator desires to provide 50% phosphine in hydrogen to the CVD deposition reactor. The operator selects this desired concentration from the software program. The microprocessor then determines the concentration of phosphine flowing through a concentration sensor. The computer program compares this concentration to the set point or desired concentration. A mass flow controller (MFC) then allows a diluting gas, hydrogen, to flow into a mixing tee where it is completely mixed with the phosphine.

20

The mixed gas then enters the concentration monitor with the mixed final concentration is determined. The MFC is then directed by the PC program to increase or decrease the diluent flow to maintain the set point concentration value. By this means, the operator can set and control any concentration between 0% and the maximum phosphine concentration produced by the generator.

30

- 17 -

I claim:

1. A method of generating high purity phosphine gas, comprising producing phosphine gas by the interaction of microwave radiation with a precursor material while said precursor material passes through a microwave transparent, metal free, gas impermeable, pressurized reaction zone.
2. The method of Claim 1 wherein the precursor material is  $\text{H}_3\text{PO}_2$  in an aqueous solution.
3. The method of Claim 1 wherein the precursor material is  $\text{H}_3\text{PO}_3$  in an aqueous solution.
4. The method of Claim 1 wherein the precursor material is crystalline  $\text{H}_3\text{PO}_2$  or crystalline  $\text{H}_3\text{PO}_3$ .
5. The method of Claim 1 wherein the precursor material is a salt of the formula  $\text{XH}_2\text{PO}_2$  in an aqueous solution where X is selected from the alkali metals group consisting of Li, Na, and K.
6. The method of Claim 1 wherein the precursor material is a salt of the formula  $\text{X}_2(\text{H}_2\text{PO}_2)_2$  in an aqueous solution where X is selected from the alkaline metals group consisting of Ca, Mg, Sr, and Ba.
7. The method of Claim 1 wherein the precursor material is a salt of the formula  $\text{XH}_2\text{PO}_3$  in an aqueous solution where X is selected from the alkali metals group consisting of Li, Na, and K.
8. The method of Claim 1 wherein the precursor material is a slurry of red phosphorus in an alkaline solution.
9. The method of Claim 8 wherein the alkaline solution is selected from the group consisting of NaOH, KOH, and LiOH dissolved in water or combinations thereof.

- 18 -

10. The method of Claim 1 wherein the high purity gas contains no more than 100 parts per million of oxygen or water vapor.
- 5 11. A chemical reactor system for generation of high purity gas, comprised of a source of microwave radiation, a microwave transparent, gas tight barrier, a microwave reflecting enclosure into which said source of microwave radiation is directed, a manifold for gas delivery adapted to receive generated gas from said enclosure, a  
10 solvent vapor removal device adapted to remove solvent vapor from the generated gas, a gas concentration sensor for sensing gas concentration in the generated gas, and a feed-back control system to control gas generation rate in said enclosure.
- 15 12. The system of Claim 11, wherein the microwave radiation source has a frequency of 0.9 GHz, or 2.41 to 10 GHz.
13. The system of Claim 11, wherein the microwave transparent barrier is constructed from materials chosen from the group Teflon,  
20 fused silica, silicon dioxide, boron nitride, or graphite.
14. The system of Claim 11, wherein the microwave reflecting enclosure is constructed from an electrically conductive material with a conductivity of a least  $10^{-3}$  ohm/cm.
- 25 15. The system of Claim 11, wherein the microwave reflecting enclosure has a smallest dimension of at least twice the wavelength of the microwave radiation.
- 30 16. The system of Claim 11 wherein the precursor material is selected from the group consisting of hypophosphorous acid, hypophoric acid, and an alkaline slurry of red phosphorous.
- 35 17. The system of Claim 11 wherein the vapor removal device contains silica gel.

- 19 -

18. The system of Claim 11, wherein the feedback control system includes a microprocessor controlled temperature feedback loop to a raw material feed pump, and microwave radiation source power supply.

5

19. The system of Claim 11 wherein the feedback control system modulates the electrical power to the microwave radiation source to maintain a constant gas delivery pressure.

10

20. The system of Claim 11 wherein the feedback control system modulates the electrical power to the microwave radiation source to provide a variable gas flow rate.

15

21. The system of Claim 11 wherein the feedback control system modulates the microwave radiation frequency to control the reaction product selectivity.

22. A concentration control system for phosphine product gas, comprising:

20

a concentration monitor for measuring the ratio of phosphine to diluting gas in a product gas stream;

a microprocessor based comparator to determine the present concentration versus a desired concentration of phosphine gas in the product gas stream; and

25

a gas flow controller to control the introduction of a diluting gas into the product gas stream in response to a signal generated based on said determination.

30

23. The system of claim 22, wherein the phosphine gas is generated by reaction of a precursor material under the influence of microwave radiation.

35

24. A method for generating a high purity gas for semiconductor processing, comprising producing the gas by the interaction of microwave radiation with a precursor material while

- 20 -

said precursor material passes through a microwave transparent, metal free, gas impermeable, pressurized reaction zone.

25. A method for fabricating a semiconductor device using a gas, characterized by the use of the gas when produced by the reaction of a precursor material under the influence of microwave radiation.

26. The method of claim 25, which comprises:  
producing the gas continuously by a continuous introduction and reaction of the precursor material in a microwave transparent reaction chamber irradiated with microwave radiation; and  
feeding the produced gas continuously as it is formed to a semiconductor fabrication process.

27. The method of claim 26, wherein the gas is continuously fed as it is produced to a chemical vapor deposition reactor or an oxidation furnace.

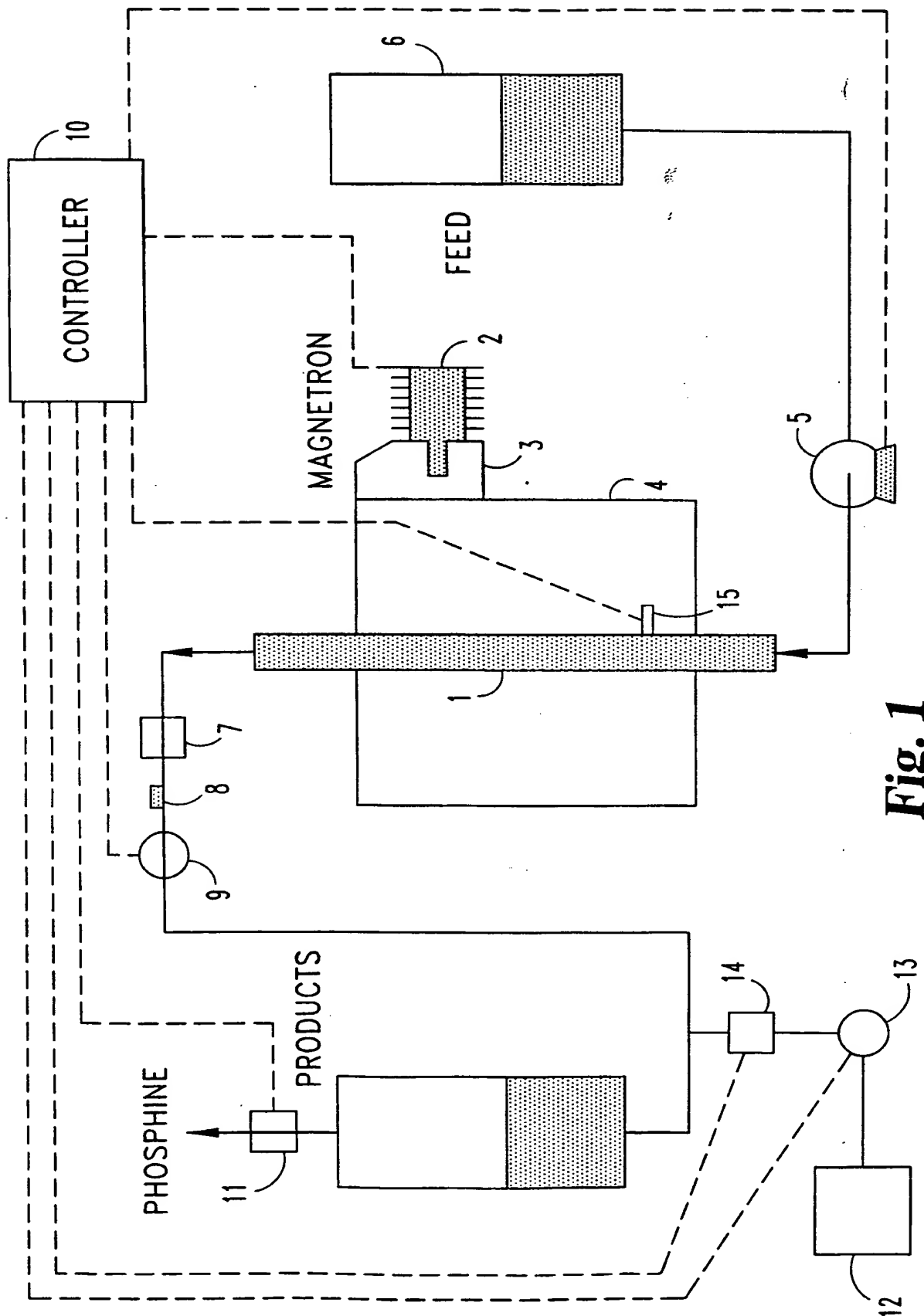
28. The method of any of claims 24-27, wherein the precursor material is liquid, and wherein the reaction produces a two-phase system including the gas.

29. The method of any of claims 24-28, wherein the gas is phosphine.

30. An apparatus for the fabrication of a semiconductor device, comprising:  
a gas generation reactor for generating a gas, the gas generation reactor having a microwave transparent reaction chamber and a source of microwave radiation directed into the reaction chamber;  
and  
a chemical vapor deposition reactor or an oxidation furnace coupled to the gas generation reactor.

31. The apparatus of claim 30, wherein the gas is phosphine.





**Fig. 1**

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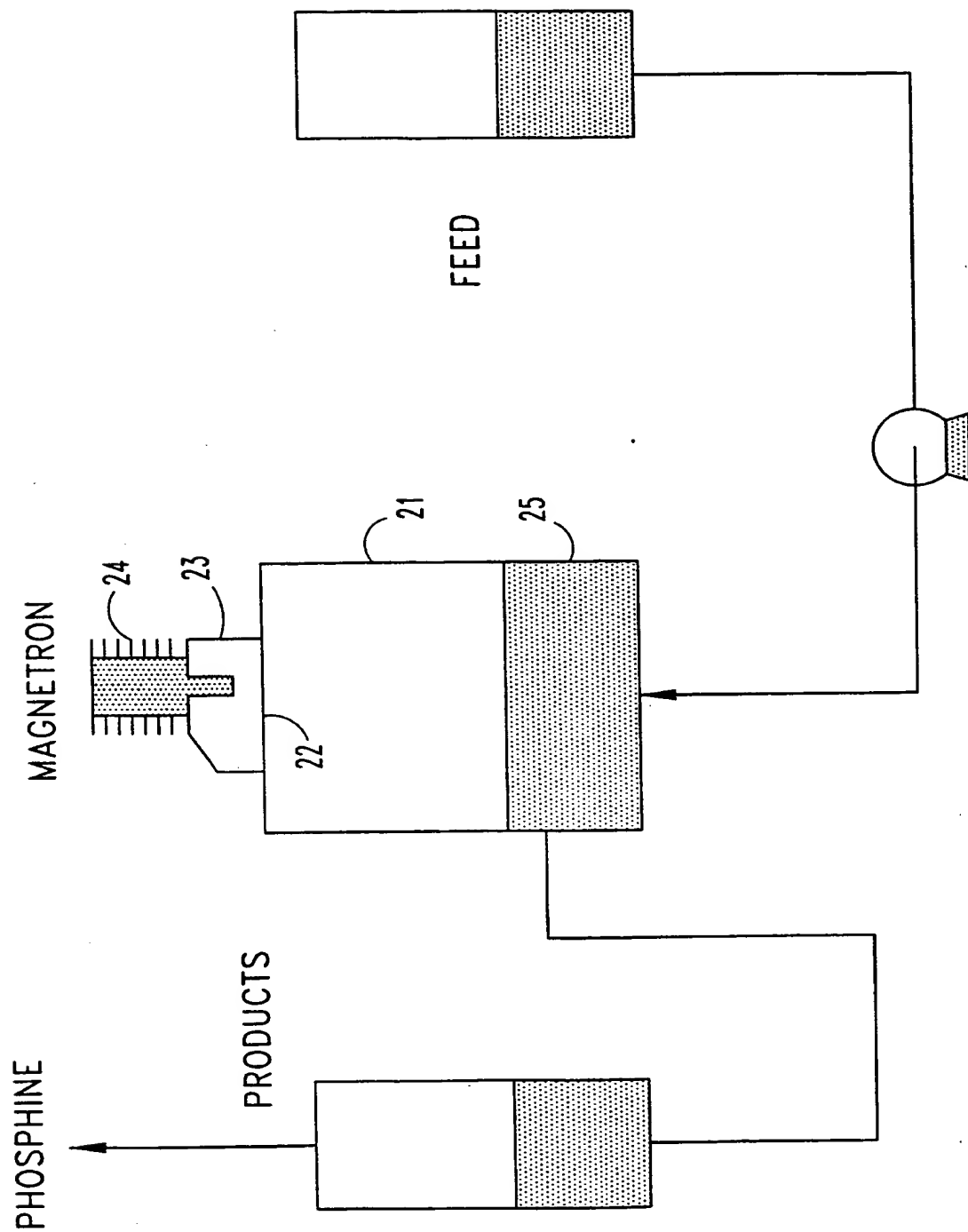


Fig. 2

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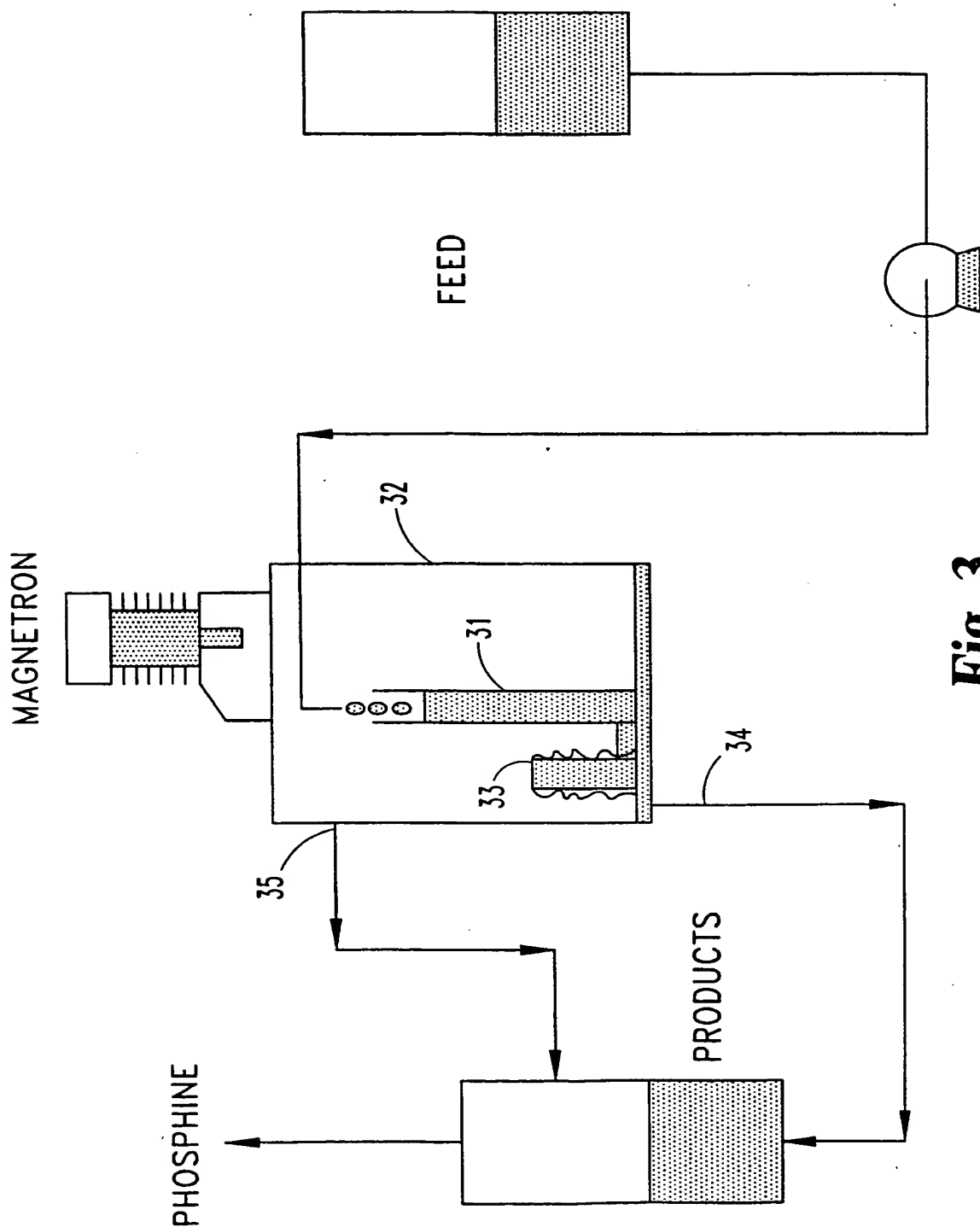


Fig. 3

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/15181

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C01B 53/00; H05B 6/50; A61L 2/00; A47J 37/08; C23C 16/00

US CL : 204/157.43; 219/707; 422/21; 96/397; 438/800, 935; 118/715

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 204/157.43; 219/707; 422/21; 96/397; 438/ 800, 935; 118/715

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST

search terms: phosphine, microwave

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,E ----- Y,E	US 5,951,831 A (GODBER ET AL.) 14 September 1999, col. 8, Example XVII.	1,3 ----- 10, 24-25
Y	US 5,569,726 A (OISHI ET AL.) 29 October 1996, col. 23, line 47 to col. 24, line 10.	2,4-9
Y	EP 454,122 A2 (KAWASAKI JUKOGYO KABUSHIKI KAISHA) 30 October 1991, page 8, line 17 to page 9, line 31 and Figs. 6-8.	11-21
X,E	US 5,925,232 A (AYERS) 20 July 1999, col. 4, lines 32-50 and Fig. 1.	22-23
Y	US 5,158,656 A (AYERS) 27 October 1992, col. 2, lines 25-40; col. 2, line 50 to col. 3, line 12; and Fig. 1.	26-31



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*B* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

20 SEPTEMBER 1999

Date of mailing of the international search report

19 OCT 1999

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer:

EDNA WONG

Telephone N (703) 308-0661

**BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING**

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-10 and 24-31, drawn to a method of generating high purity phosphine gas, a method for generating a high purity gas, a method for fabricating a semiconductor device using gas and an apparatus for the fabrication of a semiconductor device.

Group II, claim(s) 11-21, drawn to a chemical reactor system.

Group III, claim(s) 22-23, drawn to a concentration control system.

The inventions listed as Groups I-III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Group I does not require the use of the system components claimed in Groups II and III.

Group II is a microwave system.

Group III is not a microwave system.